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EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

CONTENTS.

PAGE.

Photometric Method for the Quantitative Determination of Lime and Sulphuric Acid. By J. I. D. Hinds 661
The Separation of Trimethylamine from Ammonia. By Hermann Fleck 670
Zirconium Tetraiodide. By L. M. Dennis and A. E. Spencer 673
Phthalimid. By J. A. Mathews 679
Determination of Sulphuric Acid. By N. J. Lane 682
Note on the Solubility of Bismuth Sulphide in Sodium Sulphide, with Special Reference to the Estimation of Small Amounts of Bismuth in Anti-Friction Alloys. By Thomas B. Stillman 683
On the Estimation of Sulphur in Pyrites. By G. Lunge 685
Bacteria in Milk Sugar. By Albert R. Leeds 687
The Quantitative Determination of the Three Halogens, Chlorine, Bromine, and Iodine, in Mixtures of Their Binary Compounds. By A. A. Bennett and L. A. Placeway 688
On the Inversion of Sugar by Salts. No. 2. By J. H. Long 693
Determination of Iron Oxide and Alumina in Phosphate Rock by the Ammonium Acetate Method. By Thomas S. Gladding 717
A New Method for the Estimation of Iron Oxide and Alumina in Phosphate Rock. By Thomas S. Gladding 721
Some Thoughts about Liquids. By Clarence L. Speyers 724
Volumetric Estimation of Lead. By Fred. J. Pope 737
Estimation of Sulphides in Calcium Carbide. By Fred J. Pope 740
Note on the Presence of Oil in Boiler Scale. By Charles A. Doremus 741
Occurrence of the Amines in the Juice of Sugar Cane. By J. L. Beeson 743
A Simple and Convenient Apparatus for Food-Stuff Analysis. By J. L. Beeson 744
NEW BOOKS: Chemistry for Engineers and Manufacturers; Laboratory Experiments in General Chemistry; Experiments in General Chemistry and Qualitative Analysis 745
BOOKS RECEIVED 747
OBITUARY NOTE 748
ERRATA 748

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PAPERS ACCEPTED FOR PUBLICATION:

Aluminum Analysis. By James Otis Handy.

An Analytical Investigation of the Hydrolysis of Starch by Acids. By George W. Rolfe and George Defren.

The Effect of an Excess of Reagent in the Precipitation of Barium Sulphate. By C. W. Foulk.

The Determination of Reducing Sugars in Terms of Cupric Oxide. By George Defren.

Estimation of Thoria. Chemical Analysis of Monazite Sand. By Charles Glaser.

Issued with August Number, 1896.

Proceedings.

COUNCIL.

Dr. Drown having resigned from the Committee "to unify the methods of color comparison and report on a standard for measurement of color in potable waters," the President of the American Chemical Society has appointed in his place Mr. Allen Hazen, 85 Water St., Boston, Mass. and Mr. Hazen has accepted the appointment.

CHANGES OF ADDRESS.

Bloomfield, L. M., Ohio Experiment Station, Wooster, Ohio.
Booraem, J. V. V., Box 190, Glen Cove, N. Y.
Fuller, Fred. D., Durham, N. H.
Lippincott, Warren B., North Western Iron Co., Mayville, Wis.
Mar, F. W., 138 First Ave., West Haven, Conn.
Myers, H. Ely, Carnegie Steel Co. Ltd., Lucy Furnace, Pittsburg, Pa.

MEETINGS OF THE SECTIONS.

NORTH CAROLINA SECTION.

The summer meeting was called to order at 3.30 P. M., July 7th, in the Chemical Lecture Room of the University of North Carolina. There were ten members in attendance. The secretary reported ten new applicants for membership, who were duly elected. There were other applicants who had not yet conformed to the condition of becoming members of the American Chemical Society. The membership roll has doubled in less than a half-year.

Resolutions were offered and adopted with regard to the vivisection bill and the appointment of a director-in-chief of the Scientific Bureaus of the Department of Agriculture. The following papers were then read:

"Crystallized Aluminum," by F. P. Venable; "Detection and Purification of Saccharin," by B. W. Kilgore; "Reduction

of Sulphuric Acid," by Chas. Baskerville; "Comparison of Digestibility of Raw and Steamed Cotton Seed," by J. A. Bizzell; "An Attempt to Form some Organic Compounds of Zirconium," by Thomas Clarke; "Determination of Sulphur in the Presence of Iron," by W. A. Withers and R. G. Mewborne; "Action of Phosphorus Trichloride on an Ethereal Solution of Hydrogen Dioxide," by W. A. Withers and G. S. Fraps; "Some Difficulties in the Way of the Periodic Law," by F. P. Venable.

The section then adjourned.

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PHOTOMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.[1]

BY J. I. D. HINDS.

Received May 14, 1896.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise, I found that between certain limits, an accuracy is attainable equal to that of the ordinary volumetric methods.

APPARATUS.

The only apparatus needed is a cylinder graduated from the bottom in centimeters and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made for me by Eimer and Amend. It is four cm. wide and twenty cm. high. The graduations runs to eighteen cm. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

[1] The manuscript of this article was sent similtaneously to the Chemical News and to this Journal. Owing to the absence from home of Professor Hinds, his proof was delayed too long to allow of publication of the article in the July issue.

THE METHOD.

For Sulphuric Acid.—To determine the value for sulphuric acid, I used a decinormal solution whose actual strength was one cc. equal to 0.00492 gram sulphuric acid. I took ten cc. of this solution, acidulated it slightly with hydrochloric acid, and diluted it to 200 cc. Of this solution I took forty cc., which contained 0.00984 gram sulphuric acid. To this I added enough solid barium chloride to effect complete precipitation, mixed thoroughly by pouring from beaker to cylinder and back, then measured the depth of the column through which the flame was just invisible. I then added successive portions of ten cc. water, taking the measurement after each addition. The measurement is made as follows: Hold the cylinder some twelve inches above the burning candle; looking downward through the cylinder, pour in the liquid until the image of the flame just disappears, then read the depth of the liquid. By applying the lip of the beaker to the lip of the cylinder, a very gentle stream may be made to flow in. The reading should be made two or three times so as to be sure to read the proper tenth. It is well also to enclose the cylinder in the hand, cutting off the surrounding light, so that the observation may be more accurate.

In this way I obtained the series of determinations given below. The strength of the solutions is expressed in per cent. of sulphuric acid, and is represented by y. Column 1 gives the number of the solution; column 2 the per cent. of sulphuric acid; columns 3, 4, 5 and 6 give the depth of the liquid in centimeters and tenths for four series of observations; column 7 contains the mean of these depths, expressed also by x; column 8 contains the products of these means by the percentage, also represented by xy.

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
1.....	0.0246	2.4	2.4	2.4	2.4	2.4	0.0590
2.....	0.0197	3.0	3.0	3.0	3.0	3.0	0.0591
3.....	0.0164	3.6	3.6	3.6	3.5	3.575	0.0586
4.....	0.0140	4.2	4.2	4.2	4.2	4.2	0.0588
5.....	0.0123	4.7	4.7	4.8	4.7	4.75	0.0584
6.....	0.0109	5.3	5.4	5.4	5.3	5.35	0.0583

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
7.....	0.0098	5.8	5.9	5.9	5.8	5.85	0.0573
8.....	0.0089	6.4	6.4	6.4	6.4	6.4	0.0570
9.....	0.0082	6.9	6.9	6.9	6.9	6.9	0.0566
10.....	0.0067	7.4	7.5	7.5	7.5	7.475	0.0568
11.....	0.0070	8.0	8.0	8.1	8.1	8.05	0.0564
12.....	0.0066	8.6	8.6	8.7	8.7	8.65	0.0570

I found that the continued agitation and dilution of the solutions seemed to increase the opacity, though very slightly. I therefore made another series with solutions more dilute with the following results:

No.	Per cent. sulphuric acid. y.	cm.	cm.	cm.	cm.	cm. x.	xy.
1.....	0.0098	6.1	6.1	6.0	6.1	6.075	0.0595
2.....	0.0089	6.6	6.7	6.6	6.6	6.925	0.0589
3.....	0.0083	7.2	7.3	7.3	7.3	7.275	0.0597
4.....	0.0075	7.9	7.9	7.9	7.9	7.9	0.0592
5.....	0.0070	8.5	8.5	8.4	8.4	8.45	0.0591
6.....	0.0066	9.0	9.1	9.1	9.1	9.075	0.0598
7.....	0.0061	9.6	9.6	9.7	9.7	9.675	0.0590
8.....	0.0058	10.2	10.2	10.2	10.2	10.2	0.0591
9.....	0.0055	10.8	10.8	10.8	10.8	10.8	0.0594
Mean value of xy.....							0.0593
Mean value for xy for first six of first series.....							0.0587
Mean of the two.....							0.0590

We observe that the product xy, that is, the number obtained by multiplying the per cent. of sulphuric acid in the solution by the depth of the column through which the flame is just invisible, is a constant. The curve, therefore, made by taking the one as the abscissa and the other as the ordinate is an hyperbola referred to its asymptotes, of which the equation is

$$xy = 0.0590.$$

This curve is shown in the accompanying diagram. The abscissas are centimeters and the ordinates are 0.01 per cent. to the centimeter.

Solving the equation for y, we have

$$y = \frac{0.0590}{x}.$$

To find the amount of sulphuric acid in any solution, observe

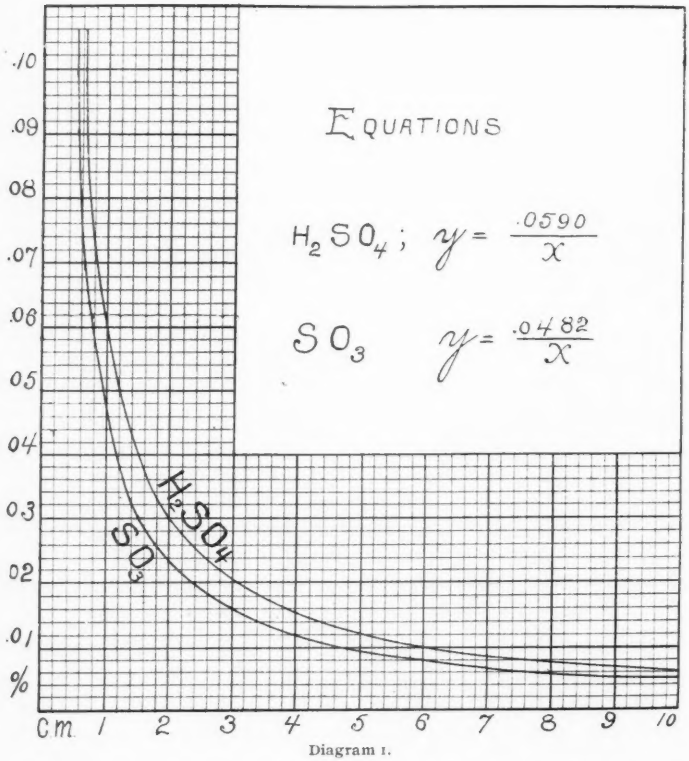

Diagram 1.

the value of x, divide this into 0.0590, the quotient will be the per cent. of sulphuric acid. Remove the decimal point three places to the right, the result will be parts in 100,000. For example, suppose the depth observed is five cm. The quotient is 0.0118. The solution, therefore, contains 0.0118 per cent. of sulphuric acid, or 11.8 parts in 100,000.

For sulphur trioxide the equation is $y = \frac{0.0482}{x}$. This curve is shown in the diagram. In the above example the amount of sulphur trioxide is 0.00965 per cent., or 9.65 parts in 100.000.

PROBABLE ERROR.

To determine the probable difference between the observed and computed values, we may compare the second set of observations above with the percentages computed from the equation. In the following table the first column contains the observed depths of the liquid, the second gives the actual strength of the solutions used, the third gives the numbers calculated from the equation, the fourth contains the difference, and the fifth the square of the difference between the numbers in the two preceding columns. The difference is represented by v.

cm.	Per cent. used.	Per cent. computed.	v.	v^2.
6.0	0.0098	0.0098	0.0000	0.00000000
6.6	0.0089	0.0089	0.0000	0.00000000
7.3	0.0082	0.0081	0.0001	0.00000001
7.9	0.0075	0.0075	0.0000	0.00000000
8.5	0.0070	0.0069	0.0001	0.00000001
9.0	0.0066	0.0065	0.0000	0.00000001
9.7	0.0061	0.0061	0.0000	0.00000000
10.2	0.0058	0.0057	0.0001	0.00000001
10.8	0.0055	0.0055	0.0000	0.00000000
			Sum Σv^2	0.00000004

By the method of least squares, the probable error is expressed in the equation

$$r = 0.6745 \sqrt{\frac{\Sigma v^2}{n-q}},$$

in which n = the number of observations, in this case 9, and q the number of constants in the equation, in this case 1. Making the substitutions, the value becomes

$$r = 0.6745 \sqrt{\frac{0.00000004}{8}} = 0.00005.$$

The probable difference then between an observed and a computed value is 0.00005 per cent., or one part in 2,000,000.

For Calcium Carbonate.—In the investigation of lime I used a solution of calcium chloride whose strength corresponded exactly to 0.001 gram of calcium carbonate to the cubic centimeter. Ten cc. of this solution was taken and diluted with twenty cc. of water, then enough solid ammonium oxalate was added to pre-

cipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of sulphuric acid. Portions of ten or twenty cc. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; column 2 shows the per cent. of calcium carbonate; columns 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; column 8 contains the means of these depths, and column 9 the product of these means by the per cents. in column 2, represented as before by xy. The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

No.	Per cent. calcium carbonate.	cm.	cm.	cm.	cm.	cm.	x.	xy.
1.....	0.0333	2.1	2.3	2.3	2.4		2.250	0.0750
2.....	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3.....	0.0100	3.5	3.6	3.5	3.5		3.525	0.0705
4.....	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5.....	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6.....	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7.....	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8.....	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9.....	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10.....	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11.....	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12.....	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13.....	0.0067	10.2	0.9	9.9	10.1	9.9	10.0	0.0670

Examining the values of xy, we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of sulphuric acid. It appears, however, to be an hyperbola, and we may assume that its equation has the form

$$xy + by = a,$$

in which b and a are constants whose values are to be determined. Substituting the values of x and y from the above table,

we obtain thirteen observation equations. The values of a and b are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained by multiplying each equation by its cofficient of b. These equations are as follows:

$0.0750 + 0.0333\,b = a$	$0.002500 + 0.001111\,b = 0.0333\,a$
$0.0718 + 0.0250\,b = a$	$0.001795 + 0.000625\,b = 0.0250\,a$
$0.0705 + 0.0200\,b = a$	$0.001410 + 0.000400\,b = 0.0200\,a$
$0.0691 + 0.0167\,b = a$	$0.001151 + 0.000271\,b = 0.0167\,a$
$0.0676 + 0.0143\,b = a$	$0.000967 + 0.000204\,b = 0.0143\,a$
$0.0669 + 0.0125\,b = a$	$0.000836 + 0.000156\,b = 0.0125\,a$
$0.0666 + 0.0111\,b = a$	$0.000740 + 0.000124\,b = 0.0111\,a$
$0.0668 + 0.0100\,b = a$	$0.000668 + 0.000100\,b = 0.0100\,a$
$0.0670 + 0.0091\,b = a$	$0.000610 + 0.000083\,b = 0.0091\,a$
$0.0666 + 0.0083\,b = a$	$0.000553 + 0.000069\,b = 0.0083\,a$
$0.0670 + 0.0077\,b = a$	$0.000516 + 0.000059\,b = 0.0077\,a$
$0.0667 + 0.0071\,b = a$	$0.000474 + 0.000050\,b = 0.0071\,a$
$0.0670 + 0.0067\,b = a$	$0.000449 + 0.000045\,b = 0.0067\,a$

Adding the equations together, we have

$$0.8886 + 0.1818b = 13a. \qquad 0.012668 + 0.003304b = 0.1818a.$$

Dividing by the coefficient of a and eliminating, we have

$$a = 0.0642 \qquad\qquad b = -0.3$$

The required equation is therefore

$$xy - 0.3\,b = 0.0642,$$

or, solving for y

$$y = \frac{0.0642}{x - 0.3}.$$

For the per cent of CaO the equation is

$$y = \frac{0.0360}{x - 0.3}.$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of x and to an axis of y three-tenths cm. to the left of the other asymptote. The abscissas are centimeters and the ordinates are 0.01 per cent. to the cm. The curves are shown in the accompanying diagram.

As an example, let us suppose that the observed depth is four and seven-tenths cm. Subtract 0.3 and divide 0.0642 by the

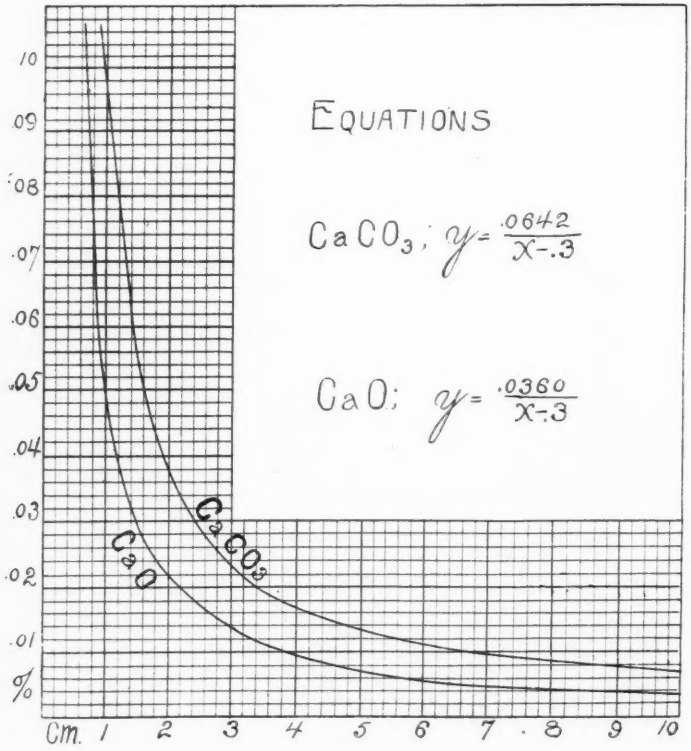

Diagram 2.

remainder. The quotient 0.0146 is the per cent. of calcium carbonate. Dividing this by 1000 we have 14.6 parts to the 100,000.

PROBABLE ERROR.

To determine the probable error of an observation we may compare as before the numbers found by observation with those computed from the equation, as follows:

x.	Strength used.	Strength computed.	v.	v^2.
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009

x.	Strength. used.	Strength. computed.	v.	v^2.
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000001
			Sum Σv^2	0.00000038

Using the same value for error as before, in which in this case n, the number of observations, is 12, and q, the number of constants in the equation is 2, we have

$$r = 0.6745\sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ per cent.}$$

That is, the probable difference between an observed and computed strength of a solution is 0.00013 per cent., or thirteen parts in ten million.

SOURCES OF ERROR.

The principal sources of error in this method are two. In the first place a light of constant intensity should be used. It makes but little difference what the light is, so it is the same as that with which the constant in the equation is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light will of course change the constants.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Any one can obtain the constants for himself by making a few determination with solutions of known strength. The best strength to use is that between 0.01 and 0.03 per cent. Great care must be used in measuring. If ten cc. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method.

PRACTICAL APPLICATION.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts.

For determining the sulphuric acid in urine I have found it quite satisfactory. The urine has to be diluted with nine volumes of water and then the color does not sensibly affect the determination.

I see no reason why this method may not be successfully used with all fine white precipitates. It is not suitable for precipitates that settle rapidly or gather quickly into flakes. Whether colored precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligation to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

CHEMICAL LABORATORY, CUMBERLAND UNIVERSITY,
LEBANON, TENN.

[CONTRIBUTIONS FROM JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 12.]

THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.

BY HERMANN FLECK.

Received May 8, 1896.

THE quantitative estimation of trimethylamine in presence of ammonia is, I believe not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes[1] prepared and analyzed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapors into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride and recrystallizing the precipitate formed several times from hot water.

[1] *Ann. Chem.* (Liebig), 81, 106.

Wicke[1] adopts the same method, using, however, alcohol-ether extract.

Winkeles,[2] in using this method, further states that while ammonium chloride is soluble to some extent in absolute alcohol, it is rendered totally insoluble by the presence of salts of such bases as trimethylamine.

Eisenberg,[3] by a similar procedure, obtained the platinum double salt in crystals of great purity and perfection.

The success in each case is undoubtedly due to the fact that large quantities of hydrochlorides were used. Winkeles,[4] for example, employed the hydrochlorides obtained from twenty-six gallons of herring brine. Further the mixtures were very rich in trimethylamine.

This method applied to a substance containing a low percentage of the latter yielded results, which clearly show that trimethylamine hydrochloride does not render ammonium chloride insoluble in absolute alcohol, and further does not serve as a good means of qualitative, much less of quantitative, separation. A portion of the mixture containing trimethylamine and ammonia was saturated with hydrochloric acid, evaporated to dryness and extracted several times with portions of several times the volume of boiling absolute alcohol. The alcoholic extract evaporated to dryness gave eighteen per cent. of supposed trimethylamine hydrochloride. To identify the latter, the residue was taken up with alcohol and platinic chloride added. The precipitate formed was redissolved in boiling water and the different fractional crystallizations, consisting of octahedra, analyzed.

	Pt found.	Required for
First crystallization.....	43.6	$(NH_4Cl)_2PtCl_4$, 43.84
Last "	39.5	Corresponding to a mixture of $2\left((NH_4Cl)_2PtCl_4\right)+3\left(N(CH_3)_3.HCl\right)_2PtCl_4$, which require 39.4 per cent. Pt.

[1] *Ann. Chem.* (Liebig), **91**, 121.
[2] *Ann. Chem.* (Liebig), **93**, 321.
[3] *Ber. d. chem. Ges.*, *1880*, 1669.
[4] *Loc. cit.*

Intermediate crystallizations gave intermediate, gradually decreasing results, showing that the isomorphous forms of the two salts crystallized together.

Duvillier, Buisine[1] extract the mixed *sulphates* to prepare pure trimethylamine from the technical product. The suggestion led to the use of the following method which yielded satisfactory results.

The mixed hydrochlorides are repeatedly extracted with portions of a total of five or six times the volume of boiling absolute alcohol and the solvent distilled off in a three-quarter liter distilling bulb. An excess of caustic soda is added to the residue and the gases formed on boiling driven over into a large quantity of water. Litmus is added, followed by the exact quantity of dilute sulphuric acid required to neutralize. The liquid is evaporated to dryness and extracted with one liter cold absolute alcohol, in which trimethylamine sulphate dissolves, leaving ammonium sulphate undissolved. The alcohol is distilled off, the residue transferred to a weighed dish, dried and weighed. In this manner 32.910 grams of the carefully dried mixed chlorides gave two and five-tenths grams trimethylamine sulphate, corresponding to 2.21 grams hydrochloride, or 6.71 per cent.

That the extraction was complete is evident from the total absence of the fishy odor when the extracted residues are treated with alkali. That the extracted material is pure is shown by the following analyses of the octahedral crystals of the platinum double salt prepared from the trimethylamine sulphate:

	Per cent. Pt.	Required for $[N(CH_3)_3.HCl]_2.PtCl_4$. Per cent. Pt.
I. 0.0983 gram gave.....	36.92	....
II. 0.3017 " "	37.12	36.93

[1] *Ann. Chem.*, (Liebig) (5) **23**, 299.

ZIRCONIUM TETRAIODIDE.

By L. M. Dennis and A. E. Spencer.

Received June 9, 1896.

WITH the exception of the tetraiodide all of the normal halides of zirconium have been prepared and described, the fluoride, chloride, and bromide being white, crystalline, sublimable solids.

A few attempts to make the iodide are recorded in the journals, but in no case was the normal compound, zirconium tetraiodide, ZrI_4, obtained. Melliss[1] passed the vapor of iodine over a glowing mixture of zirconia and carbon; he also treated zirconium tetrabromide with potassium iodide, but in neither case did zirconium tetrachloride result. Hinsberg[2] added an aqueous solution of barium iodide to a solution of zirconium sulphate, filtered off the barium sulphate, and evaporated the filtrate over concentrated sulphuric acid. He obtained a compound of the formula $Zr_2I_3O_3$, or $ZrI(OH)_3$. He also passed the vapor of iodine over a heated mixture of zirconium dioxide and carbon and states that no reaction whatever took place. Bailey[3] states that "zirconium[4] is acted upon by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained."

In the work here to be described, the authors first attempted to prepare zirconium tetraiodide by passing the vapor of iodine over heated zirconium. The zirconium first used was made by reducing zirconium dioxide with magnesium powder, the two substances being mixed in the proportion employed by Winkler[5] and demanded by the equation

$$ZrO_2 + 2Mg = Zr + 2MgO.$$

This mixture was heated in hydrogen in the usual manner and the resulting black powder was removed from the boat, thoroughly ground, and again heated in hydrogen to insure

1 *Ztschr. Chem.*, *1870*. 296: *Jsb.*, *1870*, 328.

2 *Ann. Chem.* (Liebig), **239**, 253.

3 *Chem News.*, **60**, 8.

4 Prepared by the reduction of zirconia with magnesium powder.

5 *Ber. d. chem. Ges.*, **23**, 2664; **24**, 888.

conplete reduction. To free it from magnesia, the product was treated with a saturated solution of ammonium chloride. During this treatment a gas of very disagreeable odor was evolved. It is doubtless similar to that observed by Winkler at this point. The powder was then warmed with dilute twelve per cent. hydrochloric acid and, after collecting it on a filter, it was washed with water containing hydrochloric acid, then with alcohol and ether, and finally was dried in a current of hydrogen. The analysis gave

	Per cent.
Zirconium	80.670
Silicon	0.807
Magnesium	0.117
Hydrogen	0.362
Oxygen (diff.)	18.044
	100.000

These results agree quite closely with those obtained by Winkler,[1] and indicate that the product of the reduction is chiefly zirconium monoxide rather than zirconium.

Although the powder probably contained but very little free zirconium, it was nevertheless heated in hydrogen and vapor of iodine was passed over it. An examination of the product gave no satisfactory indications, however, that an iodide of zirconium had been formed.

Inasmuch as the failure to obtain union between the zirconium and iodine might reasonably be ascribed to absence of free zirconium in the above product, it seemed advisable, before attempting any modification of the iodine treatment, to prepare zirconium by some other method and especially by some procedure in which the presence of any appreciable amount of oxygen is avoided. Under the circumstances the method of Berzelius,[2] the reduction of potassium fluozirconate with metallic potassium, seemed the most promising and was therefore employed.

The potassium fluozirconate was prepared from zircon. The zircon was finely ground, sifted through bolting cloth, and digested with concentrated hydrochloric acid until the acid gave

1 *Ber. d. chem. Ges.*, **23**, 2667.
2 *Ann. der Phys.* (Pogg), **4**, 117.

no reaction for iron. The powdered zircon, which was now almost perfectly white, was dried and mixed with four times its weight of sodium carbonate. The mixture was fused in an assay crucible furnace, allowed to cool, pulverized, and repeatedly extracted with water. The residue, consisting of zirconia and unattacked zircon together with some silica and ferric oxide, was heated with concentrated hydrochloric acid, evaporated to dryness, and heated in an air-bath to 120° to render the silica insoluble. The dried mass was treated with a little hydrochloric acid, water was added, and the silica and other insoluble matter was filtered off. The filtrate, now containing zirconium chloride and some ferric chloride, was largely diluted with water, and ammonium hydroxide was added until there was formed a slight but permanent precipitate which was then dissolved by adding as little hydrochloric acid as possible. Sulphur dioxide was then passed into the solution until the liquid smelled strongly of the gas. In many cases a precipitate of basic zirconium sulphite formed at once, but, as the compound seemed to be somewhat soluble in an excess of sulphurous acid, the solution was always boiled for from ten to fifteen minutes to insure complete precipitation. In the reaction free hydrochloric acid is formed both by the conversion of the zirconium chloride into the basic sulphite and by the reductfon of the ferric chloride to the ferrous salt. As this acid would dissolve the zirconium sulphite, it was partially neutralized by the addition, from time to time, of a few drops of dilute ammonium hydroxide. The zirconium precipitate not being wholly free from iron, it was dissolved in hydrochloric acid and again precipitated with sulphur dioxide. The pure zirconium basic sulphite thus obtained was dissolved in hydrochloric acid and zirconium hydroxide was precipitated by adding ammonium hydroxide. The well-washed hydroxide was dissolved in hydrofluoric acid, potassium fluoride was added, and the resulting potassium fluozirconate was dissolved in hot water and recrystallized.

The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form with an internal diameter of two inches and depth of five inches. The wall and

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The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form with an internal diameter of two inches and depth of five inches. The wall and

bottom are over one inch in thickness. At the top it has a flange seven inches in diameter and is provided with a cast-iron cover one inch in thickness, which can be firmly fastened to the flange by means of six one-half inch bolts.

In charging the crucible, sodium chloride, finely ground and thoroughly dried, was first put in to the depth of about an inch and a half, and this was then well pounded down with a wooden plunger to compact the salt and expel the enclosed air. On top of the salt were placed alternate layers of potassium fluozirconate, also thoroughly dried, and metallic sodium, these being pounded down as before. The remaining space in the crucible was then filled with sodium chloride and, after pounding this down, the top was bolted on and the crucible was heated for about three hours with three triple burners. This heat, however, was not sufficient to raise the crucible to redness.

The crucible was then allowed to cool and, upon opening it, the charge was found to be so compact that it had to be loosened with a chisel. On treating the mass with water the metallic zirconium, together with a small amount of the oxide which had formed, settled to the bottom while the sodium chloride and potassium and sodium fluorides dissolved.

The zirconium and zirconium oxide were separated by first floating off the lighter zirconium with water and then digesting it with dilute hydrochloric acid at 40° until all of the oxide had been dissolved. The resulting product was a black, amorphous powder which, after washing with water, alcohol, and then with ether, showed no trace of impurity before the spectroscope except a slight amount of sodium.

Vapor of iodine was passed over some of this zirconium heated to dull redness in a current of hydrogen, but with no better success than with the other sample. We then concluded to substitute hydriodic acid gas for the iodine. Considerable difficulty was encountered in finding a suitable method of preparing the gaseous hydriodic acid. That described by Merz and Holzmann[1] was finally found to answer admirably. It consists in passing dry hydrogen and vapor of iodine through a red hot tube filled

[1] *Ber. d. chem. Ges.*, **22**, 867.

with pumice stone and freeing the hydriodic acid gas from iodine by passing the gases through cotton.

In treating the zirconium with hydriodic acid gas the following apparatus was used.

Iodine was placed in a small tubulated flask connected on one side with an apparatus furnishing pure, dry hydrogen and on the other side with a long piece of combustion tubing. The half of this tube nearest the iodine flask was filled with pieces of pumice stone and rested in a combustion furnace. The other half, extending beyond the combustion furnace, was filled with cotton. The end of this tube was connected with another combustion tube resting in a second combustion furnace. The porcelain boat containing the zirconium was placed in this second tube.

The hydrogen was first passed through the whole apparatus for several hours and then the first furnace was lighted. When the pumice had become red hot the flask containing the iodine was gently heated. The tube containing the zirconium soon became filled with the hydriodic acid gas, whereupon the second furnace was lighted. As the temperature rose, a brownish-yellow substance collected in the cold end of the combustion tube, but as the heat became greater the color entirely disappeared and there remained an amorphous white sublimate. No further sublimate was formed until the tube had almost reached a bright red heat when there appeared just beyond the point where the tube was red hot a white crystalline sublimate, different in appearance from that which first formed. The gas escaping from the end of the tube contained hydriodic acid, hydrogen, some iodine, and a trace of iron, the last probably being present in traces in the zirconium and volatilizing as ferrous iodide. The tube was kept at a bright red heat for from three to four hours. The gas was then turned off and when the boat had cooled considerably the heating of the iodine flask was discontinued. The first furnace was then shut off and the whole apparatus was allowed to cool in the current of hydrogen.

The material in the boat had changed from a black to a grayish-white color, but a chemical examination showed that it contained very little iodine. The amorphous sublimate which first

formed was found not to be zirconium iodide but to contain chiefly iron and iodine.

The crystalline sublimate which was formed only at a red heat was next analyzed. These crystals were found to be insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon disulphide. They were decomposed and dissolved by concentrated sulphuric acid; they were also decomposed, but not completely, by concentrated nitric acid, iodine being liberated and a white powder, insoluble in the nitric acid, remaining. This residue was soluble in concentrated sulphuric acid and from this solution ammonium hydroxide threw down a white gelatinous precipitate. Upon dissolving this precipitate in hydrochloric acid and dipping turmeric paper into the solution, the orange color characteristic of zirconium was obtained. The solution gave no reaction for iron.

The zirconium in the compound was quantitatively determined by expelling the iodine by heating a portion of the salt with a mixture of sulphuric, nitric, and nitrous acids, dissolving the residue in concentrated sulphuric acid, diluting with water, and precipitating the zirconium with ammonium hydroxide. The precipitate was washed, dried, and ignited, and the zirconium weighed as the dioxide.

The iodine was determined by fusing some of the compound with about five times its weight of a mixture of potassium and sodium carbonate. The mass was then treated with water, filtered, and after acidifying the filtrate with nitric acid the hydriodic acid was precipitated with silver nitrate and weighed as silver iodide.

The results were

	Calculated for ZrI_4.		Found.	
	Per cent.	Per cent.	Per cent.	Per cent.
Zirconium	15.15	15.17	15.00	15.37
Iodine	84.85	85.34	85.27	....

The crystals when examined under the microscope proved to be clear, colorless cubes which showed no double refraction.

When heated for some hours in hydrogen the zirconium tetraiodide becomes black and iodine and hydriodic acid are formed. Heated in the air the iodide melts and sublimes. A weighed amount was placed in a porcelain crucible, covered with water,

and evaporated to dryness. No change in weight and scarcely any in color resulted after two such treatments. This behavior toward water is surprising, for from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colorless crystalline substance volatile at a white heat and insoluble in water or acids.

CORNELL UNIVERSITY, ITHACA, N. Y.

PHTHALIMID.[1]

BY J. A. MATHEWS.

Received June 9, 1896.

A NUMBER of years ago Prof. C. E. Colby and Mr. Dodge, of Columbia University were led to try the effect produced by heating together, under pressure, mixtures of (1) fatty acids and fatty nitrils; (2) fatty acids and aromatic nitrils; (3) fatty nitrils and aromatic acids; and (4) aromatic acids and aromatic nitrils. The reactions were carried on in sealed tubes. The score or more reactions that they tried were done at temperatures ranging from 235° to 280° C. As the result of their work they reached these conclusions regarding what is likely to take place, at least when monobasic acids and mononitrils are employed.[2]

1. Fatty nitrils and fatty acids give secondary amids.

2. Fatty nitrils and aromatic acids give fatty acids and aromatic nitrils.

3. Aromatic nitrils and fatty acids give mixed secondary amids.

4. Aromatic nitrils and aromatic acids gave secondary amids, except in one case when exceptionally high heat was used (280°) in which case the cyanide of the higher radicle was formed.

In regard to dibasic acids and dicyanides not so much has been done. Miller first tried reactions with succinic acid and ethylene cyanide.[3] He found that succinimid resulted from each of the following experiments:

[1] Read before the American Chemical Society, New York Section, June, 1896.
[2] *Am. Chem. J.*, 13, *1891*.
[3] This Journal, 16, 443, *1894*.

1. Ethylene cyanide and acetic acid heated in a sealed tube.
2. Acetonitril and succinic acid, and
3. Ethylene cyanide and succinic acid.

Some other acids in this series have been tried. Malonic acid was rather imperfectly tested. In every case the tubes exploded and malonimide was not obtained at all.

Seldner[1] reports parallel results to those obtained by Miller when he used glutaric acid and trimethylene cyanide. In the following trials which he made glutarimid resulted every time:

1. Glutaric acid (1 mol.) and acetonitril (2 mols.).
2. Glutaric nitril (1 mol.) and acetic acid (2 mols.).
3. Glutaric acid and glutaric nitril, equal molecules.

Until the writer, at Prof. Colby's suggestion, made the experiments hereinafter recorded no one, to my knowledge, had applied these methods to aromatic, dibasic acids. The results of the first experiments are very gratifying and I hope in the near future to try the reaction with other dibasic, aromatic acids.

Since no information regarding phthalic nitril could be obtained I was obliged to do without it. The experiments were therefore made with phthalic acid and propionitril.

Four sealed glass tubes each containing phthalic acid (1 mol.) and propionitril (2 mols.), plus about three drops of acetic anhydride were heated in an oven for various lengths of time and at different temperatures.

Tube I. The first tube was opened after ten hours heating at 180° C. The contents of the tube had a pungent acid odor and were treated with cold dilute potassium carbonate solution. A residue consisting of needle-like crystals remained. These were filtered off, washed with water, and dried. The crystals then had a melting point of 228° C. I immediately suspected from this melting point that phthalimid had been formed by the reaction

$$C_6H_4(COOH)_2 + C_2H_5CN = C_6H_4(CO)_2NH + C_2H_5COOH.$$

The yield of phthalimid in this experiment was about sixty per cent. of the theoretical.

[1] *Am. Chem. J.*, **17**, 1895.

Tube II. On heating the remaining three tubes higher No. 2 broke at about 215°.

Tube III. After further heating of eight hours at 200° to 215° C. the third tube was opened and the contents treated with potassium carbonate solution. The crystals remaining were not so light colored as those from Tube I, and were so different in appearance that it was thought some other reaction had taken place. The melting-point, however, was about the same as in the first case, *viz.*, 227°. Yield eighty-four per cent.

Tube IV. Exploded at 258° C.

Since the theoretical equation requires only one molecule of nitril to one of phthalic acid two more tubes were prepared, each containing equal molecules of phthalic acid and propionitril.

Tube V. After three and a half hours at 180°–200° C. the fifth tube was opened and treated with potassium carbonate solution as before. Residue crystalline; melting-point 228.5°, yield eighty-eight per cent.

Tube VI. Heated five and a half hours at 180°–200°, melting point of residue, insoluble in cold, dilute potassium carbonate solution, 228.3° C., yield 92.5 per cent.

The crystals of phthalimid were all more or less colored, the color being darkest in the case of the third tube which had been subjected to long, high heat. In no instance was any outward pressure noticed on opening the tubes.

Portions of the products were recrystallized from acetic acid, from alcohol, and from alcohol with the addition of animal charcoal to decolorize. The melting points of the recrystallized products were a little higher than before purification, *viz.*, 230°, 229.5° and 229.5°, respectively. These agree very closely with the point given in Beilstein.

Biedermann[1] gives the melting-point as 228° or 229° C.

Michael[2] gives the corrected melting-point as 233.5° C. The decolorized crystals from alcohol form beautiful long needles.

Notwithstanding the close agreement of the melting-points obtained with those given by the authorities, some other tests were made to show that the product was nothing else than

[1] *Ber. d. chem. Ges.*, 10, 1166.

[2] *Ber. d. chem. Ges.*, 10, 579.

phthalimid. A portion of the crystals heated with potassium hydroxide went into solution with evolution of ammonia. Another portion of the crystals were covered with concentrated ammonia and allowed to stand for some time. They were soon converted into microscopic crystals of phthalamid

$$(= C_6H_4(CONH_2)_2).$$

These crystals were filtered off, washed, and dried. They melted at 217.5° (uncorrected) with an evolution of ammonia, which began at about 200°. The phthalamid was further proved by its insolubility in cold water, alcohol, and ether, and by boiling it with water it was decomposed, giving off ammonia and on cooling phthalimid, melting at 230° C., crystallized out.

The results of these tests show conclusively that the product is phthalimid and that when it is made by the action of equal molecules of acid and nitril the yield is large. The reaction works comparatively readily, and at a much lower temperature than was needed to affect the reactions recorded by Colby and Dodge. It is highly probable that with slight changes of conditions any one of a variety of nitrils would give the same result. I hope to report further experiments with phthalic acid and other dibasic aromatic acids at a later day.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY, NEW YORK.

DETERMINATION OF SULPHURIC ACID.

BY N. J. LANE.

Received May 19, 1896.

SOME months ago, before hearing of the controversy between Dr. Lunge and Mr. Gladding, some experiments were made on this subject, the results of which sustain Mr. Gladding's case. The determinations were made on nearly normal sulphuric acid to establish its strength with the following results:

	Barium chloride added suddenly.	Barium chloride added by drops.
1. Sulphuric acid.....	50.03	49.23
2. " "	49.90	49.32
3. " "	50.14	....

And the average of several practically identical titrations on C. P. sodium carbonate gave sulphuric acid 49.33.

The above results were obtained with the greatest care, and every precaution used to insure accuracy. This, in my opinion, conclusively proves the accuracy of Mr. Gladding's statements.

NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN SODIUM SULPHIDE, WITH SPECIAL REFERENCE TO THE ESTIMATION OF SMALL AMOUNTS OF BISMUTH IN ANTI-FRICTION ALLOYS.

By Thomas B. Stillman.

Received June 16, 1896.

THE method of separation of lead, copper and bismuth from antimony, arsenic and tin by the use of sodium sulphide is quite general. This is dependent upon the usually accepted statement that the sulphides of bismuth, lead and copper are insoluble, and the sulphides of arsenic, antimony and tin are soluble in sodium sulphide. This process of separation is employed in the analysis of various alloys, especially of anti-friction alloys, containing lead, tin, antimony, etc.

An alloy, used for similar purposes, but containing, in addition to lead, copper, antimony and tin, a very small amount of bismuth, was recently submitted to me for analysis.

After complete solution of the alloy in hydrochloric acid with a few drops of nitric acid, the acid was neutralized with sodium hydroxide, sodium sulphide solution (1.06 sp. gr.) added and the heat applied for twenty minutes. The solution was filtered and the filtrate examined for the antimony and tin with satisfactory results.

The precipitate of insoluble sulphides remaining upon the filter was found to contain lead and copper, but no bismuth. This indicated that the small amount of bismuth which was present in the alloy had gone into solution in the sodium sulphide.

To prove this theory, I weighed 0.128 gram of pure bismuth nitrate, dissolved it in twenty-five cc. of water with a few drops of nitric acid, the clear solution neutralized with sodium hydroxide, seventy-five cc. solution of sodium sulphide added, and warmed to a temperature near boiling for twenty minutes. The solution was filtered from the bismuth sulphide, remaining insoluble in the sodium sulphide. The clear filtrate was rendered faintly acid with hydrochloric acid, when a brownish-black precipitate immediately formed. This precipitate was filtered, dissolved in

hot nitric acid and evaporated to dryness and ignited in a weighed porcelain crucible. The residue obtained was 0.031 gram of bismuth trioxide, and strongly yellow in color. It was dissolved in a few drops of hydrochloric acid, and the three following confirmatory tests for bismuth were made :

1. A portion of the solution was poured into a large amount of water, forming immediately a white precipitate of bismuth oxychloride.

2. A portion was tested by Schneider's test, the most delicate test for bismuth, the reaction obtained being strong and characteristic.

3. A portion was diluted with water, not enough to cause precipitation, and the solution saturated with hydrogen sulphide. The precipitate formed was brownish-black in color.

These three tests are absolutely confirmative of the presence of bismuth, and also show the absence of the other metals. By thus using pure bismuth nitrate for this test, lead, copper, antimony and tin are not present.

If now an analyst should weigh twelve grams of an alloy, composed approximately of lead eighty per cent., antimony fifteen per cent., tin 4.75 per cent., and bismuth 0.25 per cent. ("magnolia metal,)" and sodium sulphide solution be used for the separation of the tin and antimony from the lead and bismuth, *all* of the bismuth present would pass into solution and escape determination by the analyst.

No analyst, however, would use as much as twelve grams of such an alloy for analysis, but rather one or two grams.

If one gram be taken and sodium sulphide used as above indicated, three per cent. of bismuth might be present and *all* of it pass into solution in the sodium sulphide instead of remaining as an insoluble sulphide with the lead sulphide.

DEPARTMENT OF ANALYTICAL CHEMISTRY,
STEVENS INSTITUTE OF TECHNOLOGY.

ON THE ESTIMATION OF SULPHUR IN PYRITES.

By G. Lunge.

Received June 19, 1896.

IT has taken Mr. T. S. Gladding six months to reply to my last paper on the above subject. I will not take much more than six days from the date of receiving the May number of the Journal of before dispatching my final reply to that gentleman.

Mr. Gladding avoids any mention, and of course offers no refutation, of the charges I had brought against him, but he again puts me into a totally false light, by saying that I "attempt no further support of my position by chemical experiment." This suppresses the fact that I had referred to my more than sufficient experimental proof for Mr. Gladding's and his assistants' inability to handle my process, which has been in daily successful use by scores, if not hundreds, of chemists for a number of years past, and is that employed in Fresenius' own laboratory, as I hear from his son-in-law and laboratory chief, Dr. Hintz. Mr. Gladding now exacts a further reply from me, more especially on the strength of some new comparative tests of what he states to be the main point at issue, namely the necessity of a very slow addition of the barium chloride.

I am convinced that our readers are as tired of this dispute as I am, but as some of them might construe my silence into the admission that Mr. Gladding is right on this point, and might saddle themselves with a total unnecessary complication in their daily work, I will not shirk a further reply, although I think it unnecessary after having quoted already in March, 1895, eleven experiments by entirely independent chemists, refuting all Mr. Gladding's assertions.

In his former paper Mr. Gladding states that the error caused by the rapid addition of the barium chloride solution is from two-tenths to three-tenths per cent. of sulphur, and according to his last paper it is even one-half per cent. He appeals to independent chemists to settle this discrepancy between his statements and my own. I have taken this up in the following manner: I instructed one of my assistants, Mr. U. Wegeli, a skilled

worker, but entirely ignorant of the above dispute, to make a series of very careful tests of a sample of pyrites, just arrived for analysis and belonging to an important commercial case. I enjoined him to give me absolutely unvarnished results (which in our laboratory it would not have been at all necessary to say), and I told him, as we must be quite sure of the matter, he must not merely employ all the ordinary precautions, but also try both the usual quick addition of the barium chloride and a process recently very much recommended, namely, the very slow addition of the precipitant; I did not express any opinion of my own upon that point, and left it entirely for him to find out what there was in the matter. I had just then to undertake a short journey, and on my return he handed to me the following results.

A. *Quick* addition (*i. e.*, pouring in the hot barium chloride solution in about ten portions, occupying about half a minute in all, and stirring the mixture all the time, as every chemist would do).

1. 39.83 2. 39.65 3. 39.65 per cent. sulphur.

B. *Slow* addition from a burette, one drop per second (exactly as described by Mr. Gladding).

4. 39.63 5. 39.69 6. 39.44 per cent.

This means: In No. 2 and 3 the quick addition has given *identical* results with the slow addition in No. 4 and 5. No. 1 shows a little more, No. 6 a little less. I have suppressed nothing, and I give these results as well, although they are evidently not as reliable as the other four, entirely concordant, results; but even if we admit the less reliable results in striking an average, we find a difference of only one-tenth per cent. between the quick (39.71) and the slow (39.59) process. Such a difference is evidently within the limits of ordinary experimental error.

ZURICH.

[This discussion closes with the present paper.—ED.]

BACTERIA IN MILK SUGAR.

By Albert R. Leeds.

Received June 6, 1896.

CERTAIN phases of bacteriological investigations command universal and profound popular interest, and any publication relating to the connection of a specific organism with a zymotic disease, elicits general attention and discussion. This intimate connection of bacteriology with questions of life and death, has led many to regard the study as the proper province of medical specialists, despite the first uses made of bacteriological methods by Pasteur and his followers and to neglect them as instruments of chemical research. But the morphology, the classification, the physiology, and the botany of the bacteria are in such a rudimentary and unsatisfactory condition that the most valuable methods of bacteriological investigation are still of a chemical nature. The preparation of the culture fluids, the application of the tests, and the isolation of the products are chemical operations, and the advances to be made in the near future are to be looked for mainly on the chemical side of the subject. For this reason the absence from the columns of this Journal of papers resting upon the bacteriological questions, has been a matter of surprise to the writer, and the important contributions which have been herein recently made by Dr. Schweinitz, Dorsett, Bennett, Pammel, and Mason, a source of congratulation. Their results foretell the rich harvest of the future when the complete quantitative value of the chemical actions involved are known, and the different views which they may be expected to inaugurate as to the nature of many bodies now grouped closely together, but which deport themselves very differently when bacteria are the reagents made use of.

It is for these reasons that the writer desires to put on record the slight observations which he has made during the course of ordinary chemical work. They spring out of some anomalous behavior of specimens of milk sugar, which were being examined for purity. All the samples of pulverized milk sugar coming from the drug stores, which he examined, proved to contain a ferment when their solutions were kept at the optimum tempera-

ture for a sufficient length of time. The lactic acid produced was isolated in the form of calcium lactate. This was not the case with some lactose crystallized in nodular masses of prismatic crystals which had been obtained originally from Kahlbaum, and had been standing for twenty-five years in a stoppered jar. It was sterile. With the exception of this specimen, all the others gave an abundant crop of bacteria when definite weights dissolved in sterilized water were submitted to ordinary gelatin-peptone culture. The maximum number obtained in this medium was 1400 colonies per gram of milk sugar. In studying these colonies I looked more particularly for the bacillus *acidi lactici* and the other ten or twelve species, which are at the present time classified as the specific milk bacteria, but without success. With a lactose-litmus gelatin solution a still larger number of colonies was obtained and possibly larger search in this medium, might have revealed the specific milk bacteria of lactic acid fermentation. But my immediate object had been attained, and the presence of bacteria as a common impurity in lactose, to be looked for and avoided by the chemist and the druggist, sufficiently demonstrated.

THE QUANTITATIVE DETERMINATION OF THE THREE HALOGENS, CHLORINE, BROMINE AND IODINE, IN MIXTURES OF THEIR BINARY COMPOUNDS.

By A. A. Bennett and L. A. Placeway.

Received June 2, 1896.

CHEMICAL literature contains many records of methods for the quantitative estimation of the halogen elements, and for any one of these elements in the absence of the others they are as satisfactory as may be required. There are also, it is true, many suggestions and several proposed methods for the separation and estimation of these elements when present together or when some two are found in the same mixture, although they are generally unsatisfactory for one reason or another. The methods for qualitative determinations as given by Hart and by Kebler, in the *Journal of Analytical Chemistry*, are thoroughly satisfactory. A very convenient qualitative method that is in use

in this laboratory consists in first using chlorine water, or euchlor, (made from potassium chlorate and hydrochloric acid), which immediately determines the presence or absence of iodine and in its absence that of bromine. Carbon bisulphide is used as the final indicator. If iodine is present more chlorine water is added and the whole is heated until the iodine color is replaced by the light yellow color due to bromine. This point is easily discerned. If now one or more of these halogens are present a portion of the original solution is treated with concentrated nitric acid and boiled until both of these elements are removed. This solution is now tested for chlorine by the usual methods.

There are several methods for the quantitative estimation of the halogens by the formation of their silver salts, the further treatment depending on whether two or three of these elements are present. In all cases, however, much time is required for the analysis and great care in the manipulation of the precipitates. Sexton says, in his work on Quantitative Analysis, Third Edition, that there is no known method by which the two acids, hydrogen bromide and hydrogen chlorine can be completely separated. He recommends their precipitation as silver salts, the weighing of this product and the conversion of the bromide present into the chloride by passing chlorine gas over the fused mixtures. From the results the amount of each halogen is determined. Of course the general procedure could be used if an iodide were associated with the chloride but would not be applicable in case all three halogens were present.

Dr. Prescott, in the *Journal of Analytical Chemistry*, **3**, gives an acceptable method for the estimation of bromine in the presence of chlorine and calls attention to several others that have been employed. Fresenius gives, on pages 592 to 600 in the Second American edition of his work on Qualitative Analysis, elaborate methods for determining these elements in all possible mixtures of the binary compounds of these elements. They are generally difficult of application and employ rare reagents. It may be said, in general, that all methods of indirect estimation of the halogens in mixtures of their binary compounds are troublesome, although some of the recent modifications of these

methods give fairly satisfactory results, especially in the separation of two of the elements like chlorine from bromine.

The authors, therefore, began the examinations of several of the recent methods for the direct estimations of these elements. The method of M. Dechan was tested and found to produce too low results for the chlorine since a portion of it was set free as hydrogen chloride by the action of the sulphuric acid added after the iodin was supposed to be set free. In the original contribution[1] the author directs that the volume of the liquid in the distilling flask must not be much reduced and never below two-thirds of the original amount. Even then the amount of the chlorine is low. Under the conditions required by M. Dechan the bromine is satisfactorily separated from the chlorine and the iodine from both.

In 1885, Dr. Hart published a method for the qualitative determination of these three elements in mixtures of their binary compounds. This method suggested the method developed by the authors for the quantitative estimation of these elements.

The alkali salts of these three elements were purified and dissolved in separate solutions. The salts were taken to be pure at the start and accordingly ten grams of each of the salts was dissolved each in a liter of water. The mixtures were made from these solutions by carefully measuring definite volumes and thoroughly mixing. In this way solutions containing varying amounts of any one of the salts were prepared. The salts were afterwards found to be somewhat impure and the proper correction for this impurity has been made in the tables.

Ferric ammonium alum was used to free the iodine. The solution was made from the crystallized alum, using 200 grams to the liter. The potassium permanganate solution was a saturated solution. This was used in a concentrated form, since considerable was required to oxidize the iron that had been reduced by the iodine. The solution for the absorption of the iodine and bromine contained 200 grams of potassium iodide to the liter and thirty-five cc. were used in the receiver.

The apparatus finally found to be the best for the distillation consisted of a 500 cc. Wurtz flask with the side tube inserted

[1] *J. Chem. Soc.*, 49.

quite near the bulb of the flask. The condenser was made with a long inner tube so that it could be bent at the lower end at the proper angle to fit into the receiver. A rubber stopper was slipped on the bent end so that when the tube was inserted in the receiver it would reach into the absorbing liquid. The best receiver was a three-bulbed U tube of about 250 cc. capacity. The upper end of the distilling tube was slightly smaller than the somewhat enlarged mouth of the inner tube of the receiver so that although the former did not enter the tube yet when they were brought together and covered by a piece of rubber tubing the latter was protected from any iodine or bromine vapors. The limb of the U tube into which the bent tube of the condenser passed was stopped by a rubber stopper. In a number of the estimations a second absorption tube was attached to the usually open limb of the U tube but in no case did any recognizable amount of iodine or bromine vapor escape.

The distillations were carried on as follows: To the distilling flask was added fifty cc. of the iron sulphate solution and to this water enough to make about 200 cc. The halogen salt solutions were carefully measured from burettes into the flasks. The proper connections were made and the distillation carried on for twenty-five minutes after the liquid had reached boiling temperature. Some fifteen or twenty glass beads were added to prevent bumping. The flasks were heated by a flat four and one-half inch burner. The flask and burner were carefully protected from currents of air to prevent the drawing back of the liquid in the receiver. It was found that the rubber stopper in the distilling flask of the form indicated was not noticeably attacked by the vapors in course of about 100 determinations.

When the distillation had been completed, as just described, the flask was detached from the condenser, the tube of which was washed with a warm solution of potassium iodide followed by hot water. Another receiver prepared exactly as for the absorption of the iodine was now attached to the condenser. Thirty-five cc. of potassium permanganate solution was now added, and with it water in sufficient quantity to make the volume about 200 cc., the connections made and the distillation carried on until the bromine was all set free. Twenty-five min-

utes time was used for each distillation, but less time was usually sufficient. In fact most of the halogens were driven over during the first few minutes of heating after boiling temperature was reached. In case very great accuracy is not required an estimation can be completed in a few minutes.

It is evident that in all cases there must be relatively large excess of reagents. When the distillations were complete the iodine set free in the receiver was titrated against decinormal sodium thiosulphate. The titration can be made in the receiver but it was found most convenient to pour the liquid into a six-inch evaporating dish before estimation.

The contents of the flask are now removed to a beaker and the excess of the permanganate reduced by ferrous sulphate, adding sulphuric acid enough to render the solution clear. The solution was slightly warmed to hasten the action. It was then cooled and made up to a definite volume and an aliquot part estimated by precipitation with silver nitrate. There was nothing to prevent the estimation of the chlorine by titration, but no determinations were made by that method.

The following tables give the results of the work:

	Potassium iodide taken.	Iodine in potassium iodide.	Iodine found.	Potassium bromide taken.	Bromine in potassium bromide.	Bromine found.	Potassium chloride taken.	Chlorine in potassium chloride.	Chlorine found.
1	0.986	0.0754	0.0745	0.198	0.1330	0.1329	0.994	0.4869	0.4829
2	0.493	0.0377	0.0374	0.198	0.1330	0.1299	0.994	0.4869	0.4859
3	0.493	0.0377	0.0377	0.099	0.0665	0.0658	1.988	0.9738	0.9699
4	0.493	0.0377	0.0376	0.099	0.0665	0.0662	0.994	0.4869	0.4870
5	0.493	0.0377	0.0378	0.099	0.0665	0.0659	0.994	0.4869	0.4858
6	0.493	0.0377	0.0375	0.0495	0.0332	0.0328	0.994	0.4869	0.4867
7	0.493	0.0377	0.0375	0.0495	0.0332	0.0331	0.994	0.4869	0.4857
8	1.972	0.1508	0.1499	0.099	0.0665	0.0664	1.988	0.9738	0.9679
9	1.972	0.1508	0.1484	0.099	0.0665	0.0659	0.497	0.243	0.241
10	0.493	0.0377	0.0375	0.0495	0.0332	0.0329	0.497	0.243	0.242

The tabular statement needs no particular explanation. The quantities represented are the amounts in grams in each case.

It may be well to note that this general method is applicable for rapid technical estimations of bromine or of iodine either by themselves or in case of mixtures of the same. Single analyses can be readily made in ten to fifteen minutes.

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ON THE INVERSION OF SUGAR BY SALTS. NO. 2.

By J. H. Long.

Received June 29, 1896.

In a recent paper[1] I have shown that in their behavior with cane sugar solutions many so-called neutral salts closely resemble weak mineral acids. Salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. The same fact has been pointed out for certain salts by others, notably by Walker and Aston,[2] who determined the speed of inversion of four nitrates, comparing them with dilute nitric acid. This inversion is due to the hydrolysis of the salts in question, the hydrogen of the acids formed being in all cases, probably, the active catalytic agent.

In my former paper I gave some results obtained in a preliminary investigation on ferrous iodide with very strong sugar solutions, and in the present paper I shall give the results obtained with other salts, as well as more extended tests with the iodide.

METHOD.

In the experiments before reported I made very strong syrups containing usually fifty grams of sugar in 100 cc., and to these syrups before final dilution weighed amounts of the salts were added, the volume being brought up to 100 cc. with distilled water. In the following series of tests the amount of sugar present is much smaller, being in all cases fifty grams in 250 cc. of the finished solution. This solution is much stronger than is usually employed in inversion experiments, but with many of the salts dissolved weaker sugar solutions could not be well used. The ferrous salts, especially, require relatively large amounts of sugar to hold them in clear solution, and as many of the experiments given below were made on such salts, it was decided to employ the same weight of sugar in all cases. For each experiment, therefore, fifty grams of pure sugar was dissolved in water in a 250 cc. flask by aid of heat. The strong syrup was cooled and to it was added the salt in the powdered form or dissolved in a little water. After securing a complete

[1] This Journal, 18, 120.

[2] *J. Chem. Soc.*, July, 1895.

solution in either way, it was diluted to the mark and shaken to mix thoroughly.

The syrup so made was poured into small tubes of thin glass for inversion. These tubes held about twenty cc. and were three-fourths filled. They were cleaned for use by boiling in hydrochloric acid and then in distilled water repeatedly. After having been employed for several series of tests it was found sufficient to soak them twenty-four hours in weak acid, and then in distilled water, rinsing thoroughly finally. After receiving the sugar solutions they were closed with perforated rubber stoppers holding each a short glass tube with capillary opening. The tubes were placed in a receptacle, which was finally immersed in the water of a thermostat holding over twenty liters. The receptacle for the tubes consists essentially of two copper disks, twenty-five cm. in diameter, soldered six cm. apart on a copper rod as an axis. The lower disk is furnished with fine perforations, and the upper one with larger openings to receive the tubes. The copper axis below the lower disk ends in a hardened point, resting in a socket, and is extended above to a length of fifteen cm., ending in a grooved pulley around which a belt passes. Power applied to this belt rotates the tube receptacle, which at the same time keeps the water of the thermostat in motion. The thermostat itself consists of a large copper oven covered with asbestos boards on five sides. The top has perforations for the temperature regulator, thermometer and rotating axis of the tube receptacle. A section of the top can be quickly removed to take out tubes, but at other times should be left closed to exclude light. The capillary tubes in the stoppers closing the inversion tubes project about two cm. above the water.

With the apparatus employed it was possible to maintain a constant high temperature with a little watching through ten hours. A temperature of 85° was held with variation of less than 0.1° in either direction. With many salts the rate of inversion is exceedingly slow at ordinary temperatures, in fact almost imperceptible. For convenience in working, therefore, it was found necessary to invert at a high temperature, and 85° was

chosen. In a few instances a slightly higher temperature was employed, but the results obtained are not included below.

The reaction between the sugar and salt is probably in most instances analogous to that between sugar and weak acids, and the rate of inversion may therefore be expressed by the same differential equation:

$$\frac{dx}{dt} = K(A-x).$$

The integration of this for t and $x = 0$, together, leads to the well known formula:

$$K = \frac{1}{t} \text{ nat. log. } \frac{A}{A-x},$$

where A represents the amount of sugar present at the beginning of the inversion, x that inverted at any time, t, of an observation, and K the "constant" or "coefficient" of inversion.

As the reaction is most easily followed by means of the polaristrobometer, A is conveniently measured by the total change in rotation which is observed between the beginning of the reaction and after complete inversion. x is measured by the change of rotation from the beginning up to the time, t, of any observation. For convenience common logarithms are employed in all the calculations below. As the sugar solutions were mixed with the inverting substances at a low temperature, the intervals, t, could be reckoned only from the time when the mixtures in the tubes had reached the constant temperature of the experiment. Preliminary tests were therefore made to determine several points of practical manipulation. The thermostat was first brought to a temperature of about 87°–88°, and the filled experimental tubes and their receptacle immersed in it. From this a fall of temperature resulted, because of the low temperature of the solution. In five or six minutes the constant temperature of 85° was reached, and by regulation of the gas flame this was maintained. In another set of experiments it was found that the solutions in the experimental tubes could be brought to a temperature of 85° from the room temperature in four to six minutes. It appeared, therefore, that ten minutes was amply sufficient time to allow, after introducing the tubes into the

thermostat, before beginning the actual observations, and this was done in all cases in the experiments given below. In the case of bodies which invert but slowly there is little objection to the loss of this first ten minutes of the reaction, but in a few instances it was found to be a decided drawback, as will be seen below.

Usually 250 cc. of the solution was prepared for experiment, and this was filled into fifteen or sixteen tubes, and put into the thermostat. At the end of ten minutes a tube was withdrawn and cooled very quickly by immersion in cold water, or by holding it under a flowing hydrant. The contents were then poured into a polarization tube and polarized at the constant temperature of 20° in most cases. In a few tests made in warm weather a temperature of 25° was maintained in the dark room and in the water flowing around the observation tube. This first observation gives the initial rotation, and the time of removing the tube may be put as $t = 0$. Tubes were removed at different intervals following and treated in the same manner. The results of the polarizations were always very constant during the first few hours heating in the thermostat, as was found by removing and polarizing the contents of three tubes, but after five or six hours less regular results were found, and I adopted the plan of taking the mean result obtained by examining two or three tubes. With fifteen or sixteen tubes I made observations at eight or nine intervals.

After polarizing the liquids in the last tubes removed, the contents were mixed, returned to a tube and heated longer to obtain the end point of the reaction, that is, the point of complete inversion. The point found in this manner does not always agree with that calculated from the known weight of pure cane sugar in the original solution. Even with dilute acids the phenomenon of inversion is not as simple a thing as usually represented. As shown by Gubbe[1] and others, the specific rotation of invert sugar depends not only on the concentration, but on the time, temperature and acid used. Prolonged heating with salts produces in many cases, apparently, a slight

[1] *Ber. d. chem. Ges.*, 18, 2207.

decomposition of the levulose, from which the negative rotation of the invert sugar is found smaller than it should be theoretically. In a few instances, however, the negative rotation of the invert sugar was increased. From the experiments of Gubbe it may be calculated that fifty grams of cane sugar in 250 cc. would yield a solution after inversion, which in a 200 mm. tube should show a negative rotation of —8.6°. The rotation observed in my experiments was usually about —8.3°, but an accurate determination was not always possible, as some of the solutions became slightly colored before inversion was quite complete, and in other cases a negative rotation once observed seemed to grow slightly less on longer heating, making the exact end point somewhat uncertain. The discrepancies were not large in any case, however, and I decided to take —8.3° as the true end point for the 200 mm. tube, and —4.15° for the 100 mm. tube.

With some of the salts examined the velocity coefficient, K, is practically constant, with others it increases with the time, while in still other cases it decreases.

The sugar used in all the experiments was crystallized cut loaf of high degree of purity, and selected for the purpose. With fifty grams in 100 cc. it yields a solution of almost perfect clearness, which can be easily polarized in a 400 mm. tube. Weaker solutions yield, on inversion, results which agree perfectly with the theoretical requirement.

POTASSIUM ALUM.

Solutions of this salt invert very rapidly. A sample of pure alum was crystallized several times from distilled water to secure a product free from traces of uncombined sulphuric acid, sometimes present in the commercial article. This carefully purified salt was used in all the inversion tests. In the tables below, t refers to the time in minutes, and under α is given the observed angle of rotation in degrees and hundredths.

EXPERIMENT 1.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{64}$.

In 250 cc., fifty grams of sugar + 0.617 gram of alum.

$A = 33.03°$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.73°	....	....	....
15	20.15	4.58°	0.06483	0.00432
30	16.16	8.57	0.13045	0.00434
60	9.75	14.98	0.26243	0.00437
90	4.85	19.88	0.39998	0.00444
120	1.25	23.48	0.53891	0.00449
150	−1.30	26.03	0.67581	0.00449
210	−4.88	29.61	0.98488	0.00468
270	−6.40	31.13	1.24016	0.00459
				0.00446

EXPERIMENT 2.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{32}$.

In 250 cc., fifty grams of sugar + 1.234 grams of alum.

$A = 32.37$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	24.07°	....	....	....
15	17.83	6.24°	0.09300	0.00620
30	12.92	11.15	0.18339	0.00611
60	5.50	18.57	0.37026	0.00612
90	0.75	23.32	0.55349	0.00615
120	−2.48	26.55	0.74522	0.00621
150	−4.76	28.83	0.96114	0.00641
210	−7.00	31.07	1.39620	0.00661
270	−7.80	31.87	1.81117	0.00670
				0.00632

Experiment 3.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{16}$.

In 250 cc., fifty grams of sugar + 2.468 grams of alum.

$A = 31.25$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	22.95°	....	....	....
15	14.80	8.15°	0.13124	0.00875
30	8.79	14.16	0.26211	0.00873
60	1.07	21.88	0.52311	0.00872
90	—3.03	25.98	0.77304	0.00859
120	—5.64	28.59	1.06997	0.00891
180	—7.53	30.48	1.55533	0.00864
240	—8.15	31.10	2.31866	0.00966
				0.00886

Experiment 4.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{8}$.

In 250 cc., fifty grams of sugar + 4.936 grams of alum.

$A = 30.03$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	21.73°	....	....	....
15	11.23	10.50°	0.18686	0.01245
30	4.45	17.28	0.37205	0.01240
60	—2.87	24.60	0.74276	0.01238
90	—5.95	27.68	1.10649	0.01230
120	—7.34	29.07	1.49529	0.01244
180	—8.18	29.91	2.39838	0.01332
				0.01255

Experiment 5.

$K_2Al_2(SO_4)_4.24H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 9.872 grams of alum.

$A = 29.19$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	20.89°	....	....	....
10	10.89	10.00°	0.18216	0.01822
25	2.10	18.79	0.44820	0.01793
50	—4.70	25.59	0.90893	0.01818
90	—7.73	28.62	1.70936	0.01899
150	—8.25	29.14	2.76626	0.01844
				0.01835

An attempt was made to invert with a half normal solution but at the temperature employed the rate was found to be too rapid for accurate observation.

With the first four solutions no difficulty was found in making accurate polarimetric observations in the 200 mm. tube. The last solution, however, became finally somewhat colored, and slightly turbid from precipitation of what appeared to be aluminum hydroxide. A portion, heated 180 minutes, became too turbid for direct reading and had to be examined in the 100 mm. tube after filtration. The rotation was found now to be —3.60°, corresponding to —7.20° for the 200 mm. tube, instead of —8.25° or —8.30°. From the slight concentration due to the filtration a still greater negative value instead of a lower one should be expected. We have here an illustration of the fact referred to above, *viz.*, that prolonged heating makes the end point determination somewhat uncertain at times.

It is interesting to note the relation existing between the concentrations of the solutions and their rates of inversion in the above examples. For comparison we can call the lowest concentration unity and arrange them as follows :

Conc.		K.
$\frac{N}{64}$	1	0.00446
$\frac{N}{32}$	2	0.00632
$\frac{N}{16}$	4	0.00886
$\frac{N}{8}$	8	0.01255
$\frac{N}{4}$	16	0.01835

Inspection of the table shows that the coefficient, K, increases rapidly with the concentration, but is not directly proportional to it. It is apparent that the numbers in the third column vary approximately as the square roots of those in the second, which is clearly shown in the next table.

Conc.	K.	$K_1 \times \sqrt{\text{Conc.}}$
1	0.00446	0.00446
2	0.00632	0.00631
4	0.00886	0.00892
8	0.01255	0.01261
16	0.01835	0.01784

The regular results obtained from the aluminum salt are probably due in a measure to the inertness of the hydroxide toward sugar, as well as to the behavior of sulphuric acid in inversion. The bases of the other salts examined below form combinations with sugar more or less readily, not only with saccharose, but also with the products of inversion, so that the normal results of the reaction may be modified in a manner difficult to compute. The rather rapid rate of inversion in the above points to a relatively great degree of hydrolysis in the alum. Walker and Aston[1] found something similar in a half normal solution of the nitrate, studied at a temperature of 80°. From their polarizations a value of 0.0077 for K was found, and this was much in excess of the values found for other salts at the same time.

FERROUS SULPHATE.

A sample of the purest obtainable sulphate was recrystallized from water containing a trace of sulphuric acid, then dissolved in distilled water and precipitated by alcohol. The crystal meal secured was washed several times with alcohol and dried by fanning. The finished product was bright green and gave a nearly clear solution with pure water. It still held a trace of alcohol as disclosed by the odor. The experimental solutions were made by dissolving the sugar first and adding to this syrup the weighed sulphate meal. The mixtures were shaken to complete solution without application of heat, and then poured into the tubes for inversion. The solutions soon became turbid on warming and a minute amount of flocculent precipitate separated, making direct polarization impossible. The readings could be made therefore only after filtration, which was not without slight effect on the result. The total amount of separated hydroxide or basic salt was and remained through the test, minute.

[1] *Loc. cit.*

EXPERIMENT 6.

$FeSO_4.7H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.38 grams of sulphate.

$A = 17.12$.

t.	a.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.97	....	.....	.....
15	12.48	0.49	0.01261	0.00084
45	11.50	1.47	0.03899	0.00086
75	10.40	2.57	0.07064	0.00094
135	8.43	4.54	0.13382	0.00099
195	6.72	6.25	0.19727	0.00101
255	5.21	7.76	0.26222	0.00102
375	2.87	10.10	0.38716	0.00103
495	1.03	11.94	0.51917	0.00105
				0.00099

EXPERIMENT 7.

$FeSO_4.7H_2O$. N.

In 250 cc., fifty grams of sugar + 34.75 grams of sulphate.

$A = 17.10$.

t.	a.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.95	....	.....	.....
15	12.45	0.50	0.01289	0.00086
45	11.26	1.69	0.04520	0.00100
75	10.08	2.87	0.07980	0.00106
135	8.07	4.88	0.14593	0.00108
195	6.30	6.65	0.21388	0.00110
255	4.70	8.25	0.28606	0.00112
375	2.25	10.70	0.42682	0.00114
495	0.15	12.80	0.59953	0.00121
				0.00107

Other tests were made with a second preparation of ferrous sulphate from which the alcohol had not been as completely removed. For a half normal solution the coefficient, 0.00094, was found, and for a normal solution the value, 0.00100, both results being but a trifle lower than those obtained from the pure products. It is possible that the differences may be due to the presence of the trace of alcohol. In any case it is evi-

dent that with solutions as strong as those used the larger amount of sulphate inverts but little more rapidly than the smaller.

AMMONIUM FERROUS SUPHATE.

But one experiment was made with this salt, a very nice crystallized preparation being used.

EXPERIMENT 8.

$(NH_4)_2Fe(SO_4)_2.6H_2O$. $\frac{N}{2}$.

In 500 cc., 100 grams of sugar + 49 grams of sulphate.

$A = 17.08$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	12.93	....	.....	.....
17	12.49	0.44	0.01134	0.00066
45	11.74	1.19	0.03137	0.00069
75	10.93	2.00	0.05409	0.00072
105	10.13	2.80	0.07776	0.00074
165	8.60	4.33	0.12698	0.00077
225	7.30	5.63	0.17368	0.00077
345	4.60	8.33	0.29048	0.00084
465	2.85	10.08	0.38739	0.00083
525	2.20	10.73	0.42972	0.00082
				0.00076

The coefficient is seen to be low, but nearly a constant. In this case, as in that of the ferrous sulphate, the mixture became slightly turbid on heating.

ZINC SULPHATE.

It is practically difficult to secure a good preparation of zinc sulphate crystallized without the addition of a trace of sulphuric acid. In absence of the acid crystallization is very slow. The preparation used below was made from a chemically pure commercial sample, by crystallizing with a trace of acid first and then from pure water, after heating the solution with pure zinc. The final crystallization to secure fifty grams required weeks for its completion. In my former paper attention was called to the fact that inversion with zinc sulphate is very slow, which is well shown below. The experiment was closed when the sugar was

about half inverted, and as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period.

EXPERIMENT 9.

$ZnSO_4.7H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 17.94 grams of the sulphate.

$A = 17.25$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	13.10°	....	.....	.....
15	12.88	0.22°	0.00558	0.00037
45	12.35	0.75	0.01935	0.00043
105	11.34	1.76	0.04674	0.00044
165	10.40	2.70	0.07393	0.00045
285	8.48	4.62	0.13539	0.00048
405	6.51	6.59	0.20903	0.00052
525	4.68	8.42	0.29083	0.00055

MANGANOUS SULPHATE.

After several attempts a salt was obtained crystallized from perfectly neutral solution. Some of the crystals were so irregular in outline that it was not possible to determine from inspection whether they contained four or five molecules of water. Determination of SO_4 in the product showed, however, that a very small amount only of the latter salt was present. In making the solutions I assumed for convenience that the compound had the formula $MnSO_4.4H_2O$, and weighed out accordingly.

As I pointed out in my former paper, a solution of manganous sulphate and sugar undergoes a peculiar decomposition when heated, in which a very fine dark substance is thrown out from solution. The amount of this is so small that I could not collect enough for tests, in the work done, but it is still sufficient to make the polarimeter readings very difficult. All solutions had to be filtered before examination, but even with this precaution the readings were often obscure.

EXPERIMENT 10.

$MnSO_4.4H_2O$, $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 13.94 grams of sulphate.

$A = 34.80$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.50°	....	.....	.....
45	26.33	0.17°	0.00213	0.000047
75	26.15	0.35	0.00439	0.000058
135	25.76	0.74	0.00934	0.000069
195	25.05	1.45	0.01848	0.000095
315	22.33	4.17	0.05543	0.000176
435	19.84	6.66	0.09226	0.000212
555	16.75	9.75	0.14277	0.000257

EXPERIMENT 11.

$MnSO_4.4H_2O$. N.

In 250 cc., fifty grams of sugar + 27.88 grams of sulphate.

$A = 34.75$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.45°	....	.....	.....
15	26.25	0.20°	0.00250	0.00017
45	26.00	0.45	0.00566	0.00013
75	25.75	0.70	0.00883	0.00012
135	24.90	1.55	0.01981	0.00015
195	23.00	3.45	0.04541	0.00023
315	18.20	8.25	0.11770	0.00037
435	14.45	12.00	0.18397	0.00042
555	9.50	16.95	0.29053	0.00052

EXPERIMENT 12.

$MnSO_4.4H_2O$. $2N$.

In 250 cc., fifty grams of sugar + 55.76 grams of sulphate.

$A = 34.42$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	26.12°	....	.....	.....
30	25.12	1.00	0.01280	0.00043
90	22.80	3.32	0.04405	0.00049
150	17.82	8.30	0.11984	0.00080
220	12.33	13.79	0.22231	0.00101
338	4.60	21.52	0.42622	0.00126
450	0.27	25.85	0.60383	0.00134
570	—3.80	29.92	0.88360	0.00155

EXPERIMENT 13.

$MnSO_4.4H_2O$. $3N$.

In 250 cc., fifty grams of sugar + 83.64 grams of sulphate.

$A = 34.00$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.70°	....	....	....
30	24.22	1.48°	0.01933	0.00064
90	18.76	6.94	0.09915	0.00110
150	11.50	14.20	0.23481	0.00156
220	4.75	20.95	0.41587	0.00189
338	—2.69	28.39	0.78252	0.00232
450	—6.25	31.96	1.22185	0.00272
570	—8.05	33.75	2.13354	0.00363

The rates of inversion cannot be directly compared in the above experiments because the latter were not carried to completion. In the first case over one-third of the sugar originally present was inverted, in the second case almost exactly one-half, in the third case about six-sevenths, while in the last case the inversion was very nearly complete. By plotting the results it is possible to determine approximately the rate of inversion when just one-half of the sugar has been inverted and this I have done. The results are given below, and show that the coefficients, K, are nearly proportional to the concentrations, these being referred to that of the half-normal solution as unity.

Conc.	K.
1	(0.00032)
2	0.00054
4	0.00109
6	0.00172

The first coefficient, 0.00032, is uncertain because it was found by a rather wide extrapolation, but between the others there is fair agreement.

MANGANOUS CHLORIDE.

The salt used was purified by several crystallizations from the best obtainable Schuchardt product.

EXPERIMENT 14.

$MnCl_2.4H_2O$. $\frac{N}{4}$.

In 250 cc., fifty grams of sugar + 6.18 grams of chloride.

$A = 35.00$.

t.	α.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	26.70°	....	....	....
15	26.60	0.10°	0.00124	0.00009
45	26.30	0.40	0.00499	0.00011
75	26.00	0.70	0.00878	0.00012
135	25.25	1.45	0.01838	0.00014
255	22.66	4.04	0.05327	0.00021
375	18.75	7.95	0.11190	0.00030

The high initial rotation here is very extraordinary, corresponding to a specific rotation of 66.75°.

EXPERIMENT 15.

$MnCl_2.4H_2O$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 12.35 grams of chloride.

$A = 34.84$.

t.	α.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	26.54°	....	....	....
15	26.45	0.09°	0.00113	0.00008
45	26.16	0.38	0.00476	0.00011
75	25.85	0.69	0.00869	0.00012
135	24.52	2.02	0.02594	0.00019
255	22.26	4.28	0.05693	0.00022
375	17.15	9.39	0.13639	0.00036
495	13.00	13.54	0.21370	0.00043
555	11.52	15.02	0.24498	0.00044

EXPERIMENT 16.

$MnCl_2.4H_2O$. N.

In 250 cc., fifty grams of sugar + 24.70 grams of chloride.

$A = 34.63$.

t.	α.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	26.33°	....	....	....
15	26.12	0.21°	0.00264	0.00018
30	25.86	0.47	0.00593	0.00020
60	25.15	1.18	0.01505	0.00025
120	23.05	3.28	0.04321	0.00036
180	20.07	6.26	0.08659	9.00048
300	15.60	10.73	0.16105	0.00054

EXPERIMENT 17.

$MnCl_2.4H_2O$. 2*N*.

In 250 cc., fifty grams of sugar + 49.40 grams of chloride.

$$A = 34.18.$$

t.	α.	*x*.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.88°	....	....	....
15	25.38	0.50°	0.00640	0.00043
45	23.91	1.97	0.02578	0.00057
75	22.21	3.67	0.04933	0.00065
135	18.25	7.63	0.10971	0.00081
195	14.80	11.08	0.17016	0.00087
345	5.25	20.63	0.40183	0.00116

No very plain relation can be found connecting these rates of inversion. The coefficients corresponding to the time of completion of one-third of the inversion are here given.

Conc.	*K*.
1	(0.00038)
2	0.00041
4	0.00055
8	0.00088

The first coefficient had to be estimated and is uncertain.

FERROUS CHLORIDE.

Considerable difficulty was experienced in preparing a solution of ferrous chloride devoid of traces of free acid. A weighed excess of pure iron wire was covered with water in a small flask and then the calculated volume of titrated hydrochloric acid was added in amount just sufficient to produce the solution of required strength. The mixture was gently warmed and allowed to stand a short time. Warming was repeated at intervals through several hours, until the liberation of hydrogen became very feeble. The solution so obtained stood five days in the presence of the excess of iron, being boiled twice in the interval, and was then filtered cold into the sugar solution, which was made up to the proper volume with fresh distilled water.

The actual strength of solutions made in this manner was determined by titration later. The two following were almost exactly normal and half-normal.

Both solutions became turbid on heating and had to be fil-

tered before polarization for the first tests. After the lapse of about two hours the cloudiness disappeared and the solutions then taken from the thermostat were clear enough for direct polarization.

EXPERIMENT 18.

$FeCl_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 7.925 grams of chloride.

$A = 16.18$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	12.03°	....	....	....
15	9.47	2.56°	0.07507	0.00500
45	7.44	4.59	0.14517	0.00322
105	5.00	7.03	0.24783	0.00236
165	3.83	8.20	0.30725	0.00186
285	1.90	10.13	0.42749	0.00150
405	—0.50	12.53	0.64696	0.00160
525	—2.01	14.04	0.87884	0.00167

EXPERIMENT 19.

$FeCl_2$. N.

In 250 cc., fifty grams of sugar + 15.85 grams of chloride.

$A = 15.71$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	11.56°	....	....	....
15	9.40	2.16°	0.06424	0.00428
45	6.88	4.68	0:15360	0.00341
105	4.75	6.81	0.24679	0.00235
165	3.56	8.00	0.30913	0.00188
285	1.15	10.41	0.47190	0.00165
405	—1.42	12.98	0.76002	0.00187
525	—3.25	14.81	1.24194	0.00236

These results are very surprising, inasmuch as they show but little difference between the rates for the two concentrations. In both instances the rates rapidly decrease from the beginning and after the sugar has been about half inverted they increase a little. I give next some results from solutions which had not been boiled so thoroughly, and which may have held a little free acid.

EXPERIMENT 20.

$FeCl_2$. 0.52N.

In 250 cc., fifty grams of sugar + 8.242 grams of chloride.

$A = 34.00$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.70°	....	....	....
15	20.00	5.70°	0.07969	0.00531
45	12.80	12.90	0.20720	0.00460
75	9.00	16.70	0.29343	0.00391
105	6.19	19.51	0.37041	0.00353
165	2.42	23.28	0.50129	0.00304
285	—1.95	27.65	0.72771	0.00256
345	—3.96	29.66	0.89399	0.00258
405	—5.30	31.00	1.05436	0.00260

EXPERIMENT 21.

$FeCl_2$. 0.98N.

In 250 cc., fifty grams of sugar + 15.53 grams of chloride.

$A = 33.60$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.30°	....	....	....
15	19.84	5.46°	0.07702	0.00513
45	14.20	11.10	0.17416	0.00387
75	11.80	13.50	0.22314	0.00297
105	9.88	15.42	0.26675	0.00254
165	7.65	17.65	0.32358	0.00196
285	1.45	23.85	0.53734	0.00188
345	—1.50	26.80	0.69383	0.00201

The effect of free acid is not apparent. Six other experiments were made with normal and half-normal ferrous chloride solutions, the results of which were very similar to those above. In all cases the constant was found to increase before the completion of the inversion.

The constant for 0.001 N hydrochloric acid was determined for comparison at the same temperature, $t = 85°$, and with the same amount of sugar. It was found

$K = 0.0051$.

FERROUS BROMIDE.

Solutions of this salt were made by adding the proper amount

of bromine to an excess of iron and water. A reaction soon begins which is hastened by heat. Finally the solution is thoroughly boiled, which eliminates all free bromine and leaves the iron in the ferrous condition. It is then filtered into the cold sugar solution and is ready for use. A solution so made is practically neutral.

EXPERIMENT 22.

$FeBr_2$. 0.54 *N*.

In 250 cc., fifty grams of sugar + 14.58 grams of bromide.

$A = 31.43$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	23.13°	....	....	....
15	16.76	6.37°	0.09836	0.00655
45	9.76	13.37	0.24062	0.00534
75	6.07	17.06	0.33988	0.00453
105	4.00	19.13	0.40743	0.00388
165	0.68	22.45	0.54406	0.00329
285	—4.03	27.16	0.86691	0.00304
345	—5.60	28.73	1.06598	0.00309

EXPERIMENT 23.

$FeBr_2$. 1.04 *N*.

In 250 cc., fifty grams of sugar + 28.08 grams of bromide.

$A = 29.50$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	21.20°	....	....	....
15	13.60	7.60°	0.12938	0.00862
45	6.22	14.98	0.30785	0.00684
75	2.90	18.30	0.42060	0.00561
105	0.75	20.45	0.51317	0.00489
165	—2 70	23.90	0.72163	0.00437
285	—6.35	27.55	1.17979	0.00414
345	—7.50	28.70	1.56673	0.00454

The normal solutions here invert but little faster than the half-normal. The rates in both cases diminish rapidly from the start, but after the middle of the inversion become nearly constant, as was observed with the ferrous chloride. The first three of the solutions taken from the thermostat had to be filtered before polarizing.

FERROUS IODIDE.

A half-normal solution was made by mixing 15.87 grams of iodine with an excess of iron and water, in the usual manner. On complete disappearance of the iodine the solution was boiled and filtered into a cold sugar solution. Water was finally added to make the volume up to 250 cc. The amount of sugar present is not sufficient to prevent some decomposition on heating, but, as in the other cases referred to, the turbidity at first noticed disappeared after longer warming in the thermostat. The first polarizations were made after filtering, and those later were made directly.

EXPERIMENT 24.

FeI_2. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 19.37 grams of iodide.

$A = 32.03$.

t.	α.	x.	$\log.\frac{A}{A-x}$.	$\frac{1}{t}\log.\frac{A}{A-x}$.
0	23.73°	....	....	....
15	17.45	6.28°	0.09478	0.00632
30	13.57	10.16	0.16571	0.00552
45	11.62	12.11	0.20627	0.00458
60	9.73	14.00	0.24956	0.00416
90	7.50	16.23	0.30690	0.00341
150	4.40	19.33	0.40176	0.00268
270	0.90	22.83	0.54177	0.00200
390	—2.80	26.53	0.76520	0.00196

In my former paper a preliminary experiment with ferrous iodide was described in which the coefficient appeared to be nearly constant and much smaller than here. The experiments are, however, not comparable, as in the former case the sugar solution was very strong, containing, in 250 cc., 125 grams of sugar. In such a solution the degree of dissociation of the iodide would be necessarily very different from that in a weaker solution. In the strong solution no separation of ferrous hydroxide or other compound appears, even on warming. A strong syrup is much more stable than a weak one, and the lower rate of inversion may be thus easily accounted for.

CADMIUM CHLORIDE.

One solution of cadmium chloride was tested as to its inverting power. It was made with a salt purified by several crystallizations at a low temperature, free from uncombined acid.

EXPERIMENT 25.

$CdCl_2$. $0.94N$.

In 250 cc., fifty grams of sugar + 42.958 grams of chloride.

$A = 29.71$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	21.41°	....	.....	.....
15	12.80	8.61°	0.14862	0.00990
30	6.59	14.82	0.30001	0.01000
60	—1.33	22.74	0.62967	0.01049
90	—4.89	26.30	0.94015	0.01044
150	—7.70	29.11	1.69475	0.01129

The rate of inversion is about as rapid as with $0.002N$ hydrochloric acid at the same temperature and same sugar concentration.

LEAD NITRATE.

A single test was made with a solution containing lead nitrate. The salt was recrystallized from a pure Schuchardt specimen and was weighed in proper amount directly.

EXPERIMENT 26.

$Pb(NO_3)_2$. $\frac{N}{2}$.

In 250 cc., fifty grams of sugar + 20.65 grams of nitrate.

$A = 33.70$.

t.	α.	x.	$\log. \frac{A}{A-x}$.	$\frac{1}{t} \log. \frac{A}{A-x}$.
0	25.40°	....	.....	.....
15	22.86	2.54°	0.03403	0.00227
45	17.38	8.02	0.11803	0.00262
75	12.10	13.30	0.21800	0.00284
135	2.28	23.12	0.50314	0.00372
195	—3.63	29.03	0,85831	0.00440
345	—7.70	33.10	1.74948	0.00507

The coefficient here is found to increase very rapidly, as was noticed by Walker and Aston in their experiments,[1] which were

[1] *Loc. cit.*

carried out with a half normal nitrate solution at 80°, but with a weaker sugar solution. The mean value they give from the results of polarization at three intervals is 0.00159, but the inversion was not carried nearly to completeness, as in the above case.

The experiments given show in a marked manner the extreme variations in the value and constancy of the inversion coefficient and the data obtained may be roughly tabulated as follows:

Potassium alum	K constant.
Ferrous sulphate	" increases slowly.
Ammonium ferrous sulphate	" " "
Zinc sulphate	" " "
Cadmium chloride	" " "
Manganous sulphate	" " rapidly.
Manganous chloride	" " "
Lead nitrate	" " "
Ferrous chloride	" decreases rapidly.
Ferrous bromide	" " "
Ferrous iodide	" " "

In the cases of the last three salts the values of K decrease very rapidly at the beginning of the heating, but become nearly constant later, finally, in fact, appearing to increase a little. This behavior seems to bear some relation to the stability of the salts in aqueous or weak saccharine solution. As was mentioned these ferrous halogen solutions became turbid in the thermostat, and the first three or four portions withdrawn in each case for polarization had to be filtered. Later, the liquids became perfectly clear under the influence of longer heating.

During the turbid stage of the reaction, owing to the temporary separation of a trace of base in insoluble form, the amount of free acid present would be relatively increased, and would therefore greatly accelerate the speed of inversion. With the clearing of the solutions on longer heating the normal hydrolysis only would obtain and then the reaction should approach in regularity that due to the presence of a small constant amount of mineral acid.

It was mentioned that the solutions with ferrous sulphate and ferrous ammonium sulphate became likewise turbid on heating. But here the very slight opalescence persisted through the

whole time of heating, and was perhaps greater at the end of the reaction than at the beginning. Other experiments also show in this respect a marked difference between ferrous sulphate and chloride. In my former paper I referred to solutions of these salts which had been used qualitatively. Portions of these solutions that had not been heated are still in existence. After standing eight months in the light I find that the chloride is practically clear, while the sulphate has become much changed. The bottle contains a decided flocculent precipitate. My former experiments with a strong solution seemed to indicate that at a temperature of 100° the first slight precipitate which forms disappears, but this is not true of the weaker solutions at 85°.

The slight precipitate of ferrous chloride and other halogen compounds being temporary, while that of ferrous sulphate is apparently permanent, we should expect just such irregularities in the speed of inversion, as the experiments actually show. A solution of manganous sulphate with sugar becomes also slightly decomposed on heating, and the decomposition increases with the time and temperature. At a temperature of 100° a solution of fifty grams of sugar and ten grams of the sulphate in 100 cc. becomes so dark that an exact polarization is not possible, even after filtering. The solution in the present case is much less concentrated, but the precipitate is still marked and its formation is undoubtedly attended by the separation of a little free acid. We should therefore expect an acceleration in the rate of inversion as before.

These considerations do not aid us in explaining, however, the increase in K for manganous chloride, cadmium chloride or lead nitrate. The solutions with these salts are clear and remain so throughout the reaction. In the case of manganous chloride it must be remembered that an almost complete loss of color follows after heating. The pink fades, and in a few hours at the temperature of the thermostat becomes imperceptible in a small volume of the liquid. The color is not restored by cooling. We have here evidently a reaction in which a change takes place in the form of combination of the manganese, with a necessary alteration in the degree of dissociation of the salt.

It is true, as already said, that most of the bases under consideration form compounds with the sugars, so that we should expect from this cause a slight disturbance at least in the apparent rate of inversion. Too little is known of the optical properties of these saccharose, dextrose and levulose metallic compounds to say just what effect they would have on the rotation, but that they have some action is suggested by the results of some of the polarizations to determine the end point in the inversion. This was usually found a little below the theoretical, —8.6° for a 200 mm. tube, but in several cases it was found above after prolonged heating. This was also true of a solution of sugar with manganous chloride, which stood exposed to the light several months.

It must be remembered also that solutions of dextrose are easily oxidized, and those of levulose much more so. The dark color often seen near the end of the reaction, points to such a decomposition.

It will be recognized that a determination of the hydrolysis of many of the heavy metallic salts cannot be measured with great accuracy, because of these several disturbing influences, but a comparison of some little value in the above cases may be made by considering the results obtained at the beginning of the reactions in which the coefficient is an increasing one, and near the end of the reaction in cases where it decreased and then became nearly constant. By taking the mean of the first two values in the one case, and of the last two in the other, we obtain the second column of the table below as the most probable values of the coefficient for half-normal solutions.

In the third column is given a calculation of the extent of hydrolysis of the salts, expressed in per cents. of total salt present, and based on a comparison with hydrochloric acid acting in 0.001 normal solution at the same temperature on same amount of sugar. This comparison is at best a rough one, assuming as it does complete hydrolysis of the acid, and neglecting the effect of the excess of undecomposed salts on the rate of inversion.

	K.	Salt hydrolyzed in per cent.
Lead nitrate	0.00244	0.096
Manganous chloride	0.00095	0.035
Manganous sulphate	0.00052	0.020
Ferrous sulphate	0.00085	0.033
Ferrous ammonium sulphate	0.00068	0.026
Zinc sulphate	0.00040	0.016
Ferrous chloride	0.00164	0.063
Ferrous bromide ($0.54N$)	0.00300	0.109
Ferrous iodide	0.00198	0.078
Potassium aluminum sulphate, $\frac{N}{4}$	0.01835	1.440
Cadmium chloride $0.94N$	0.01000	2.080

The amount of hydrolysis is small in all cases except those of the alum and cadmium chloride.

My thanks are due to Mr. S. R. Macy for much assistance in the experimental work of the above.

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DETERMINATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK BY THE AMMONIUM ACETATE METHOD.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE oldest method of separating alumina and iron phosphates from lime phosphate is, probably, the ammonium acetate method. This has been severely criticised, and just at present seems to be under condemnation. The following investigation has convinced the writer that, when properly carried out, not only does the method give an accurate separation of iron and alumina from lime phosphate, but also gives a neutral phosphate of uniform composition from which the iron oxide and alumina present may be accurately estimated.

In brief, the method used is this. If a weakly acid solution of phosphates of iron and alumina together with a large amount of calcium phosphate be slowly poured into a strong solution of ammonium acetate made acid with acetic acid, the iron and alumina are precipitated as phosphates, upon digestion for a short time at a gentle heat. This precipitate, however, con-

tains more or less calcium phosphate, which is removed by several reprecipitations. I shall demonstrate by experiment:

First, That upon continued reprecipitations of iron and alumina as phosphates in this manner, there is no appreciable diminution of the quantity of either finally obtained, provided there always be a large excess of phosphoric acid present.

A standard solution was made by dissolving twenty grams of ammonia alum (C. P.) in distilled water. This was slightly acidified with hydrochloric acid, in order to prevent the alumina from separating on standing, and diluted to one liter. This solution, upon being standardized, was found to contain the theoretical amount of alumina, that is,

Ten cc. = 0.0225 grams Al_2O_3.

One precipitation, in the manner described above, of the alumina in ten cc. gave

	$Al_2O_3.P_2O_5$, found.	Al_2O_3.
1	0.0545	0.0228
2	0.0549	0.0229
3	0.0546	0.0228
4	0.0540	0.0226
5	0.0545	0.0228

Three successive precipitations, in which one gram of ammonium phosphate was added before each precipitation, gave

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0550	0.0230
2	0.0547	0.0229
3	0.0544	0.0227

Five successive precipitations were also tried under the same conditions, with the following results:

	$Al_2O_3.P_2O_5$.	Al_2O_3.
1	0.0536	0.0224
2	0.0530	0.0222

When, however, the excess of phosphoric acid was omitted before the reprecipitations, there was a loss of alumina.

An iron solution was made by dissolving C. P. iron wire in hydrochloric acid and oxidizing it with nitric acid. When carefully standardized it was found that

Ten cc. = 0.0296 Fe_2O_3.

Three successive precipitations, adding one gram ammonium phosphate before each, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0545	0.0289
2	0.0550	0.0291
3	0.0548	0.0290

Five successive precipitations, in the same way, gave

	$Fe_2O_3.P_2O_5$.	Fe_2O_3.
1	0.0550	0.0291
2	0.0560	0.0297

Second. That upon three successive precipitations in the presence of a large amount of calcium phosphate, as is the case in the analysis of rock phosphate, the precipitate of the phosphates of iron and alumina is sufficiently pure to be taken as such. Of the standard solutions, five cc. of each would together give a precipitate of combined phosphates about equal to that usually found in one gram of phosphate rock. The mixture so analyzed was made up as follows:

Five cc. alumina solution = 0.01125 Al_2O_3.
Five cc. iron solution = 0.01480 Fe_2O_3.
0.7000 grams calcium phosphate.

This was given three precipitations, the excess of phosphoric acid being supplied before the second and third precipitations.

	Phosphates obtained.	Al_2O_3 obtained.	Fe_2O_3 obtained.
1	0.0552	0.0115	0.0146
2	0.0540	0.0110	0.0146
3	0.0537	0.0109	0.0146
4	0.0536	0.0109	0.0146

The iron oxide was determined by volumetric method in the ignited precipitate and the alumina by subsequent calculation.

In addition twenty cc. alumina solution containing 0.0450 grams Al_2O_3, together with 0.700 grams calcium phosphate, were given three successive precipitations in the same way with the following results:

	$Al_2O_3.P_2O_5$ obtained. Grams.	Al_2O_3 obtained. Grams.
1	0.1092	0.0456
2	0.1074	0.0449

In order to prove that the aluminum phosphate precipitated was the normal phosphate, the ignited precipitates were fused, and the phosphoric acid in them estimated.

	$Al_2O_3.P_2O_5$.	P_2O_5 obtained.	Al_2O_3 by diff.	Al_2O_3 by calc.
1	0.0538	0.0313	0.0225	0.0225
2	0.0533	0.0312	0.0221	0.0223

The phosphate of alumina is multiplied by the factor 0.418 to obtain the alumina.

Therefore, in determining iron oxide and alumina in phosphate rocks proceed as follows:

Four grams of the finely ground sample, previously freed by a magnet from any metallic iron derived from the iron mortar used in grinding the sample, are digested for half an hour, at a temperature just below the boiling-point, with about thirty cc. dilute hydrochloric acid (1–1). This will prevent the solution of any pyrites if present. Filter and wash thoroughly into a 200 cc. flask, add a little nitric acid, and boil to oxidize the iron, cool, and fill to mark with water. Take two portions, fifty cc. = one gram, twenty-five cc. = one-half gram, and proceed with each as follows:

Almost neutralize the solutions with strong ammonium hydroxide until the precipitate formed dissolves with difficulty, and thoroughly cool by placing the beaker in a dish of cold water. The neutralization is then completed by carefully adding dilute ammonium hydroxide until the precipitate remains permanent, then just dissolve by adding dilute hydrochloric acid, drop by drop, stirring well. Have ready in another beaker a mixture of fifteen cc. of a strong solution of ammonium acetate (made by neutralizing thirty per cent. acetic acid with strong ammonium hydroxide) and five cc. of acetic acid. Carefully pour the cold faintly acid solution of phosphates in a fine stream into this mixture, stirring all the while. Digest at 60° C. from one-half hour to one hour, until the supernatant liquid is clear and the flocculent precipitate is well settled to the bottom.

Filter and wash the precipitate once with a ten per cent. ammonium acetate solution, merely rinsing out the beaker in which the precipitation was made. Dissolve the precipitate from the paper into the same beaker with a few cubic centimeters of hot dilute hydrochloric acid (1–4). Use as little acid as possible in order to keep the bulk of the solution small. Add one gram of ammonium phosphate, neutralize with ammonium

hydroxide and add hydrochloric acid until the precipitate just dissolves as before and pour into a mixture of fifteen cc. ammonium acetate solution and five cc. acetic acid. Digest at 60° C. for one-half to one hour and filter, and wash once with the ten per cent. ammonium acetate solution. Redissolve and repeat the precipitation, being careful to again add one gram of ammonium phosphate to the solution, in order that there be a sufficient excess of phosphorus pentoxide to precipitate all the alumina as a neutral phosphate. Wash the precipitate three times with dilute ammonium acetate solution.

Take the filter, while wet, from the funnel and ignite in a tared platinum capsule, using a very low flame until the filter paper is thoroughly charred. The heat is increased gradually until the paper is completely consumed, and finally the blast lamp is used for a minute. Weigh as combined phosphates of iron and alumina. The iron is determined volumetrically in the solution of the weighed precipitates. The iron oxide present in the rock is also determined separately by volumetric process, preferably the bichromate method, in a solution of five grams of the rock in dilute hydrochloric acid (1–1), reducing all iron to protoxide and titrating with bichromate.

The ignited precipitate from one of the duplicate precipitations may, if desired, be dissolved and subjected to a fourth precipitation and the filtrate tested for lime by adding ammonium oxalate and heating. My thanks are due to our assistant, Thomas Brown, Jr., for valuable aid in the above analytical determinations.

LABORATORY OF STILLWELL & GLADDING,
NEW YORK CITY.

A NEW METHOD FOR THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK.

BY THOMAS S. GLADDING.

Received June 30, 1896.

THE method for the separation of alumina from phosphate of lime by three successive precipitations with ammonium acetate is tedious, though accurate if proper precautions be taken, as shown in the preceding paper on this subject.

The following modification suggested itself as saving both

time and labor. This modification consists of the separation of alumina from calcium phosphate and iron by means of its solubility in an excess of caustic potash. To demonstrate the accuracy of this method, a solution of ammonia alum, twenty grams in a liter, was used as in the previous experiments, ten cc. containing 0.0225 grams Al_2O_3. The caustic potash solution was made by dissolving 500 grams of caustic potash in distilled water and diluting to one liter. Chemically pure caustic potash, purified by barium, was used and was carefully tested for alumina, as much so-called chemically pure potash contains an appreciable amount of alumina.

To a solution of mixed phosphates of alumina, iron, and lime were added fifteen cc. of the C. P. potash solution. The mixture was digested for an hour at a temperature of 70° C., with occasional stirring. It was then filtered, the filtrate neutralized with hydrochloric acid, and the alumina was precipitated as a phosphate with ammonium acetate as described in my ammonium acetate method.

Ten cc. standard alumina solution + 0.030 gram iron oxide + 0.500 gram calcium phosphate gave

	$Al_2O_3.P_2O_5$ found. Grams.	Al_2O_3. Grams.
1	0.0538	0.0225
2	0.0542	0.0227
3	0.0543	0.0227
4	0.0543	0.0227

Comparative tests were made on phosphate rocks between this method by solution in C. P. potash and by three successive precipitations with ammonium acetate.

	By new potash method. Al_2O_3 found. Per cent.	By acetate method. Al_2O_3 found. Per cent.
1	1.05	1.03
2	1.19	1.16
3	1.86	1.61
4	1.07	0.99
5	1.88	1.98

These results show the accuracy of this method, both in obtaining a known amount of alumina and in showing close agreement with results by the acetate method.

This method has been in use in our laboratory for over a year. A reprint of an article by M. Henri Lasne[1] has just been received, giving a method for the separation of alumina from phosphates of iron and lime very similar to this. M. Lasne uses caustic soda instead of potash and precipitates his aluminum phosphate with ammonium hyposulphite instead of ammonium acetate. I have made a few comparative tests by my method and that of M. Lasne and find closely agreeing results.

Using ten cc. standard alumina solution + 0.500 grams calcium phosphate I found

	By my method.		By Lasne's method.	
	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.	$Al_2O_3.P_2O_5$. Grams.	Al_2O_3. Grams.
1	0.0542	0.0220	0.0540	0.0226
2	0.0538	0.0225	0.0533	0.0223

In the analysis of a phosphate rock I found

By my method. Al_2O_3 found. Per cent.	By Lasne's method. Al_2O_3 found. Per cent.
1.75	1.73
1.80	...

The detailed method used in my work is as follows: Treat the finely ground rock phosphate with a magnet to remove any metallic iron derived from the iron mortar used in the preparation of the sample. Dissolve four grams of the rock in thirty cc. dilute hydrochloric acid (1–1), heating just below the boiling-point for half an hour. This prevents the solution of pyrites. Filter into a 200 cc. flask, add a few drops of nitric acid, and boil to oxidize the iron, cool and dilute to mark. Take fifty cc. containing one gram of rock and run into twenty cc. of the solution of C. P. caustic potash. Digest for an hour at 70° C., stirring occasionally. Let the precipitate settle and filter on a large paper, first decanting the supernatant liquid on the paper and finally washing on the precipitate. Wash two or three times with hot water.

To the filtrate add one gram of ammonium phosphate, acidify with hydrochloric acid, add ammonia until a permanent precipitate is formed and dilute hydrochloric acid, drop by drop, until it is just dissolved. Add a mixture of fifteen cc. neutral ammo-

[1] From the *Bulletin de la Société chimique de Paris*, [3] **15**, 118, *1896*.

nium acetate solution and five cc. acetic acid (thirty per cent.) and digest for half an hour at 70° C., by which time the precipitation is complete.

Filter, washing five or six times with hot ammonium acetate solution (ten per cent.), stirring up the precipitate with the jet each time. Ignite with a low flame until the paper is charred, increase the heat, and, when the paper is completely consumed, blast for a minute. The precipitate is the normal aluminum phosphate and its weight multiplied by the factor 0.418 gives the Al_2O_3.

The iron oxide is determined volumetrically, preferably by the bichromate method, in a solution of the precipitate of iron oxide and calcium phosphate thrown down by the caustic potash. It is also determined separately, by the same method, in a solution of five grams of the rock in dilute hydrochloric acid (1–1).

My thanks are due to Mr. H. E. Cutts, A.M., for valuable assistance in the above investigation.

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NEW YORK CITY.

SOME THOUGHTS ABOUT LIQUIDS.

BY CLARENCE L. SPEYERS.

Received June 3, 1896.

CONSIDER an empty closed space. Imagine a quantity of liquid put into it, enough to fill the space with vapor and leave some liquid over. A portion of the liquid changes into vapor and passes into the previously empty space above the liquid and continues doing so until the pressure of the vapor reaches a certain value, when the vaporization ceases.

The usual way of explaining this vaporization starts out by assuming that, with the exception of the surface, the liquid is perfectly homogeneous in a physical sense. That is, there is not a single particle of the liquid which for any appreciable length of time is different from any other particle, but of course, spaces between the particles of liquid are recognized. At the surface of the liquid, however, a distinction is to be made. For outside the surface, the activities are different from those within the surface, otherwise there would be no boundary. So that the

particles at the surface are subjected to activities that are different in different directions, and consequently the particles so situated will behave differently from those particles entirely within the liquid.

In van der Waal's theory the mutual attractions of the particles of the liquid are considered as the restraining force to keep the particles more or less together. This assumed force must be very great—a good many hundred atmospheres. Inside the liquid, below the surface, the attraction is equal in all directions, but at the surface it acts only in one direction, inwards, normal to the surface. Now, although the force restraining the particles of liquid from separating is so great, yet the theory of common acceptance assumes that some particles do break away from the mass of the liquid and form vapor. The liquid is said to evaporate. It is hard to accept this view of the case, particularly as electrical results point towards an exceedingly quiet condition of affairs within the body of liquids.

Still admitting that the particle does break away from this attraction, it cannot do so without an abundant supply of energy, which must be accounted for. It does not seem right to find this energy in the heat of vaporization, for a particle of liquid will voluntarily take heat energy from the liquid to do this work, and so go off as a particle of vapor at the sacrifice of the energy of the liquid.

It is not possible to prevent a liquid from vaporizing by refusing to give it heat; it will take the required heat from the rest of the liquid. In other words, the condition of the liquid state strongly favors vaporization.

The common theory tries to get over this difficulty by claiming that the particle which gets away, gets away by virtue of an inherent kinetic energy greater than the attractic energy of the particies of liquid, that is, greater than the force denoted by van der Waal by $K = \frac{a}{v^2}$, and that it possesses this excess of kinetic energy in the body of the liquid, before it got away, and that it got away only by virtue of this excess of kinetic energy. Similarly with all particles in the liquid having a kinetic energy

greater than the energy of the mutual attraction of the particles the one for the other.

Still again admitting that the particles with the greater kinetic energy do succeed in getting out, we shall have to look for a loss in the mean kinetic energy of the liquid, to be shown by a fall in temperature. This is the case and in this respect theory and fact agree, for vaporization lowers the temperature of the liquid. In regard to the vapor, however, we meet with this difficulty. The kinetic energy of a given particle while within the liquid might be just sufficient to carry it beyond the sphere of action of the liquid, in which case the kinetic energy remaining to the particle after reaching freedom would be little and its temperature should be less than that of the liquid; on the other hand, the kinetic energy of the given particle might be far more than sufficient to carry it beyond the sphere of action of the liquid and then the kinetic energy that the particle still has after reaching freedom, should be more or less great. Consequently a particle of vapor, just after getting out of the liquid, might have any temperature between absolute zero and ∞°, in some cases perhaps touching the inferior limit, but of course, never reaching the superior limit. As a consequence of this we should expect to find the temperature of the vapor very different from that of the liquid; but this is not the case, observation has never shown that the temperature of the vapor is very different from that of the liquid which produces it. However, this is not a fatal objection, for we can assume that the mean of kinetic energy, while within the liquid, of the particles that escape from the liquid is of just such a value that after they have all got out of the liquid, the diminution of their mean kinetic energy, due to the attraction of the liquid, brings the kinetic energy left to them to the mean kinetic energy of the liquid. This seems like a forced explanation, very forced, but still perhaps not more so than the theory it is intended to help.

However, we are not yet out of the difficulty. For what becomes of the kinetic energy lost by the particles as they pass out into the vapor state?

So far as the liquid is concerned, it may take the form of heat energy and so lessen the quantity required to supply the deficit

due to the escape of the particles with great kinetic energy from the liquid. But all of the lost kinetic energy cannot be absorbed here in the liquid, some must also go into the vapor particles. It may take the form of heat, as we have suggested in the case of the liquid, but then we have to assume that the kinetic energy, while within the liquid, of the particles that escape is of just such a value that, after they have all got out of the liquid, the diminution in their mean kinetic energy, due to the attraction of the liquid plus this correction, brings the kinetic energy left to them to the mean kinetic energy of the liquid, which is absurd.

Nor does the attractive energy seem to be stored up as potential energy, as in the case of a stone raised above the surface of the earth, for there is no evidence at all that a vapor particle tends toward the liquid as the stone does toward the earth. When the particle gets out of the liquid it seems to be utterly indifferent to the liquid.

Of course the mutual attraction that all bodies have for each other is left out of account.

Nor is there any sign of electrical action, at least if the experiments made up to the present time are conclusive.

There are then a good many very serious objections to the present theory of vaporization.

First, in accounting for the escape of the vapor.

Second, in accounting for the temperature of the vapor.

Third, in accounting for the kinetic energy lost by the particle in getting through the surface of the liquid and beyond the sphere of action of the liquid particles.

Let us now turn our attention to another view of the case. Consider a liquid which has no vapor-tension of its own, a non-volatile liquid, but which can dissolve gases. The liquid and gas are supposed to act according to Henry's law, that is, the ratio of concentration of the gas in the liquid part and in the gaseous part is to be constant, or in other words, the quantity of gas dissolved by the liquid is to be proportional to the pressure on the gas.

In such a system there are three constituents to be considered. The gas in the gaseous state, the gas in solution, and the solvent.

The state of the dissolved gas is not positively known, but in all probability it is in a state corresponding to a gas under high pressure for these reasons. In the first place, it is hard to see how a substance like nitrogen, for example, could be in the liquid state in a solution of moderate concentration. Great pressure is required to liquefy it even when the temperature is far below the ordinary temperature, and at the ordinary temperature it has hitherto been found impossible to liquefy nitrogen, no matter how great the pressure. Still it would be consistent with the ordinarily accepted theory to claim that the attraction of the particles of solvent could overcome the great internal energy of the gas particles and bind them down to a lesser activity and produce the liquid state. But on the other hand, modern investigation has very plainly shown that dissolved substances have a gaseous nature; the particles of the dissolved body are free to assert their physical individuality. That is to say, the solvent is to be considered rather as a medium through which the dissolved body can be put under certain conditions, the conditions varying to some extent with each solvent, but all solvents having the common action of allowing a sort of gasification of the substance dissolved, In general the solvent is not to be considered as a substance which unites with the dissolved body, forming a new compound. For example, consider anhydrous calcium chloride. When this is treated with water there is strong evidence of combination of the two to form calcium chloride hydrate. If the quantity of water is properly adjusted the whole of it combines with the calcium chloride, forming a crystallized hydrate. If this crystalline substance is treated with more water, solution begins and during this process, which is the real solution, there is no sign of chemical action. It is true, some scientists, particularly those of the English school, have denied this and have claimed to find strong evidence of a chemical action during the process of solution, but so far all such claims have turned out to be mere opinions based upon very doubtful measurements.

So we are to look upon solution as being a change in which the dissolved body is gasified. Sometimes a further change, electrolytic dissociation, takes place, but that is outside the

scope of this article. It is in best accordance with what we know about other bodies to assume that the dissolved nitrogen is in the form of a gas, and to recognize two states in the solution, the gaseous state of the substance in solution and the liquid state of the solvent.

Let us now pass on to a liquid which gives off vapor. The purpose of this article is to justify the view that this vapor behaves toward the liquid just as the nitrogen did toward its solvent in the previous case, of course, with the obvious limitations due to identity in the composition of vapor and liquid.

The boundary dividing vapor from liquid is commonly supposed to be at the surface of the liquid, although the possibility of a differentiation occurring inside the liquid does not seem to be denied, for so far as could be found out by the writer, the question of such a possibility has never been raised.

The tendency for a liquid to vaporize and the pressure of its saturated vapor is evidently a function of temperature only. There seems to be no reason, therefore, why the fluid should not separate into vapor and liquid within the surface of the liquid. That it is possible for vapor to be there follows from what we know about the gaseous nature of the substances in solution. It is rather odd that this view of the case was not adopted at the outset by chemists.

According to this view, when we heat a liquid we increase the energy of translatory motion, we increase its temperature. But besides this we cause a separation of some of the liquid particles from the body of the liquid, bringing them into a state of freedom, such that they can behave just as the particles of any other substance would do in the same solvent. This of course will consume considerable energy. These free particles of vapor in the liquid we shall call dissolved vapor particles. So that on heating in liquid we produce dissolved vapor and raise the temperature of the whole fluid; possibly we do more, but at any rate we do these two things. Now by Clausius' theory of the true specific heat, the heat required to raise only the temperature of a unit mass of substance one degree, should be the same whatever the state of the substance may be, and the value of the true specific heat should be the value of the specific heat when

the substance is in such a state that the heat added can only change its temperature and not do any other internal work, namely when the substance is in a state of gas. So if we subtract from the specific heat of the liquid the specific heat of the gas, the remainder should be the heat consumed in other internal work, and if no other internal work is done than the rise in temperature and production of dissolved vapor, we should get the heat required to change some of the liquid into dissolved vapor. The quantity changed into vapor however is so far unknown.

The dissolved vapor is supposed to be produced until its energy balances the energy of the liquid part.

Suppose, for example, we heat one gram of water one degree in a closed vessel which does not allow it to give off gaseous vapor. The heat required will be about one calorie, depending upon the initial temperature; one calorie is near enough for our purpose. A part of the heat goes to increase the translatory motion and is the true specific heat; but another part, perhaps the whole of the remainder, we claim goes to produce dissolved vapor. Subtracting the true specific heat of water, namely the specific heat of water vapor at a high temperature = 0.4776, we have left 0.5224 as the heat required to change a certain unknown quantity of water into dissolved water vapor, provided that no internal work is done but the two kinds we have considered. We shall assume this to be true until there is evidence of a more complex change.

Now suppose a space be made over the liquid, to let a certain quantity, say one per cent., be changed into gaseous vapor. It is of course evident, if the theory be at all tenable, that the vapor arising from the liquid comes from the dissolved vapor and bears to the dissolved vapor the same relation that the nitrogen did to the dissolved nitrogen. Comparatively little heat should be required in this process, for most of the change has been effected in the body of the liquid. Whatever is required here should be looked upon as the true heat of vaporization; that which is usually so called we are to consider as including the heat required to change a unit mass of liquid into dissolved vapor as well as the heat required to vaporize the unit mass of dissolved

vapor. The two quantities should evidently be kept carefully separated.

Let us now proceed to determine the concentration of the dissolved water vapor. As the dissolved water vapor is supposed to be like a dissolved gas, Henry's law should give us some aid in finding the quantity. We might assume, in the first place, that the relative vapor density of a liquid at two different temperatures gives the relative osmotic pressures of the dissolved vapor at those temperatures, were it not for the uncertainty as to how the temperature affects the pressure of the vapor and the osmotic pressure of the dissolved vapor. It would not do to assume that each was affected in the same degree by a change in temperature. But our theory does allow us to claim in the case of a given liquid at a constant temperature that two different vapor-tensions will correspond to two different concentrations of the dissolved vapor by Henry's law, and that the relative vapor-tensions are as the relative concentrations of the dissolved vapor. Now we can change at will, within quite a wide range, the vapor tension of a liquid without changing its temperature and without introducing any complications.

To understand this let us refer back to the original conception of the dissolved vapor. If we have liquid water in a vessel with any number of gases under moderate pressure, the partial pressure of the saturated water vapor will be very nearly the same as if it alone were present in the space containing the gases. So when we dissolve a substance in water it would seem as if we might argue that the osmotic pressure of the dissolved substance should not affect the pressure of the dissolved water vapor. However the conditions in the two cases are very different. In the first case there is abundant space for the water vapor so that all that is necessary is time for the concentration of the water vapor to reach the same value no matter how many gases may be present, provided of course that the total pressure be not very great. When however the total pressure is great, the vapor-tension of the liquid diminishes very much. This is just the condition that holds in a liquid. The volume available for a dissolved substance is very small, and so anything put into this space will very materially lessen the space available for the dis-

solved vapor, particularly as the quantities used in solutions are generally very much greater than those used in the gaseous state.

Suppose we have n gram-molecules of a substance whose molecules do not dissociate on dissolving, say sugar, and dissolve it in water. Let ν be the number of gram-molecules of dissolved vapor after the n gram-molecules of substance have been dissolved, then the total number of gram-molecules present in solution will be $\nu + n$, and the relative number of gram-molecules of substance dissolved to total number of gram-molecules in solution is

$$\frac{n}{\nu + n}.$$

Now let j be the concentration of the dissolved vapor when alone in the liquid, and j' its concentration after the new substance has been added, in this case the sugar. $j - j'$ will be the decrease in the concentration of the dissolved water vapor due the addition of the n gram-molecules of sugar, and since a gram-molecule of all substances occupies the same volume, the decrease in concentration $j - j'$ will be the same whatever the substance dissolved may be, provided the same number of gram-molecules be taken in each case, or the decrease in concentration of the dissolved vapor is proportional to the number of gram-molecules dissolved in a certain fixed volume of solution. If the temperature is constant the concentration of the dissolved water vapor cannot rise above the value j, which it has when only dissolved vapor is present; when we try to get above this value the dissolved vapor turns to liquid water. Hence the number of gram-molecules in a unit volume must be fixed, if the temperature is constant, that is

$$\nu + n = \text{constant}.$$

We have, therefore,

$$\frac{j - j'}{j} = \alpha \frac{n}{\nu + n} \qquad (1)$$

where α is a constant.

$j - j'$ can be calculated by van't Hoff's law, and n is known, but the other quantities are not, so neither j or ν can be calculated from this equation.

There is however another relation that can be deduced.

The concentration of the dissolved vapor is measured by its osmotic pressure.

Let π, ϕ, be respectively osmotic pressure and osmotic volume of the dissolved vapor, when it alone is present; π', ϕ', the corresponding quantities when a substance is in solution; p, v, the pressure and volume of the vapor in contact with the pure solvent; p', v', the corresponding quantities when a substance is in solution.

Consider an isothermal reversible cycle composed of the following parts.

By means of a semipermeable diaphragm let a gram-molecule of dissolved vapor pass from the pure solvent, the work will be

$$-\pi\phi = -RT.$$

Let the gram-molecule of vapor expand until it has a pressure of π the work will be

$$-\int_{\pi'}^{\pi} \phi d\pi = -RTl\frac{\pi}{\pi'}.$$

Let it then pass into the solution; the work will be

$$+\pi'\phi' = +RT.$$

Let x gram-molecules pass out of the solution in the form of vapor; the work will be

$$-xp'v' = -xRT,$$

where x denotes the number of gram-molecules of gaseous vapor necessary to make one gram-molecule of dissolved vapor.

Let the x gram-molecules of vapor be compressed until the pressure equals p; the work will be

$$+x\int_{p'}^{p} vdp = +xRTl\frac{p}{p'}.$$

Let the x gram-molecules be driven into the pure solvent; the work will be

$$+xpv = +xRT.$$

Thus the cycle is completed. The quantity of solution is supposed to be so large that the addition and removal of the quantity of the solvent used in the cycle will have no appreciable effect upon the concentration of the solution.

The sum of the changes of energy must be zero, so

$$-RT - RTl\frac{\pi}{\pi'} + RT - xRT + xRTl\frac{p}{p'} + xRT = 0;$$

Hence,
$$\frac{\pi}{\pi'} = \left(\frac{p}{p'}\right)^x \tag{2}$$

We shall assume that x equals 1; there is no good reason for thinking otherwise, and the simplicity in the structure of dissolved bodies favors this assumption.

From the theory we have

$$\frac{j}{j'} = \frac{\pi}{\pi'} \tag{3}$$

We have therefore from 1 through 3 and 2,

$$1 - \frac{p'}{p} = \frac{p - p'}{p} = \alpha\frac{n}{\nu + n} \tag{4}$$

but from experiment,

$$\frac{p - p'}{p} = \frac{n}{N + n} \tag{5}$$

where N is the number of gram-molecules of liquid in which n gram-molecules of substance have been dissolved.

Hence,

$$\alpha\frac{n}{\nu + n} = \frac{n}{N + n} \tag{6}$$

Now as equation (6) is true for any small value of n it will be true for a value so small in comparison with ν and N, that it may be neglected, and so

$$\frac{\alpha n}{\nu} = \frac{n}{N},$$

or,

$$\alpha = \frac{\nu}{N} \tag{7}$$

Substituting in (6) we have

$$\frac{\nu}{N}\,\frac{n}{\nu+n}=\frac{n}{N+n},$$

or,

$$\nu = N \tag{8}$$

That is, the concentration of the dissolved vapor is the same as the concentration of the liquid, or in other words, all the solvent is to be considered as dissolved vapor.

This is very interesting, for it is in effect the same conclusion that van der Waals reached in his celebrated treatise, though he pursued a very different method.

It would seem from this result that matters were left in about the same state that they were in at the outset; that the view of dissolved vapor was no better than the old view, which claimed that the change into vapor took place only on the surface of the liquid. But we have really gained several things.

In the first place we have found that reasoning from the analogy that a dissolved gas and the same gas in contact with the solvent bears to the liquid and its vapor we got to the idea of dissolved vapor and from that to a result in agreement with a much older theory.

Secondly, we have found that a liquid is to be looked upon as a condensed gas, not simply condensed in the sense that it is a matter compressed into smaller space, but condensed in the sense that the gaseous activity, pressure, is carried into the liquid condition, and we are to treat a liquid as we would a gas.

Thirdly, it follows from this view that a substance dissolved is simply brought into the same condition that the liquid is in, and consequently should have the same property of exerting an osmotic pressure that the liquid has.

Finally, what causes the condensed gaseous state? Until this is answered the problem of liquid and gas is essentially unsolved. That it is due to an attraction between the molecules, is hardly possible, as we have seen at the beginning of this paper. Indeed so soon as we begin to reflect upon the complications that are introduced the moment the ideas of molecule and attraction are brought into an investigation, and these complications are all

the time increasing instead of diminishing, the more natural and simple appears the view of Ostwald that we shall find a better solution of such problems in energy alone, matter being only a collection of energies in space.

Now as to the value of the osmotic pressure in some liquids.

In 1000 cc. of water there are

$$\frac{1000}{18} = 55.55 \text{ gram-molecules.}$$

Every gram-molecule at 25° C. (= 298° absolute temperature) in 1000 cc. has a pressure of

$$\frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \text{ m.}$$

Hence for the 55.55 gram-molecules of water we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{18} = 1024 \text{ meters of mercury.}$$

In 1000 cc. methyl alcohol there are

$$\frac{1000}{32} \cdot 0.79 \text{ gram-molecules,}$$

and hence for methyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{32} \cdot 0.79 = 455 \text{ m.}$$

In 1000 cc. ethyl alcohol there are

$$\frac{1000}{46} \cdot 0.79 \text{ gram-molecules,}$$

and hence for ethyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.79 = 316 \text{ m.}$$

In 1000 cc. propyl alcohol there are

$$\frac{1000}{60} \cdot 0.80 \text{ gram-molecules,}$$

and hence for propyl alcohol we have

$$\pi = \frac{22222}{1000} \cdot \frac{298}{273} \cdot 0.76 \frac{1000}{46} \cdot 0.80 = 249 \text{ m.}$$

In 1000 cc. chloroform there are

$$\frac{1000}{119}.\ 1.52 \text{ gram-molecules,}$$

and hence for chloroform we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{119}.\ 1.52 = 235 \text{ m.}$$

In 1000 cc. toluene there are

$$\frac{1000}{92}.\ 0.88 \text{ gram-molecules,}$$

and hence for toluene we have

$$\pi = \frac{22222}{1000}.\frac{298}{273}.\ 0.76\frac{1000}{92}.\ 0.88 = 176 \text{ m.}$$

RUTGERS COLLEGE.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE SCHOOL OF MINING, KINGSTON, ONTARIO.]

VOLUMETRIC ESTIMATION OF LEAD.

BY FRED. J. POPE.

Received May 21, 1896.

QUITE frequently of late, the attention of readers of chemical journals has been directed to various methods[1] for estimating lead volumetrically. But, while some of these methods are superior to any previously made public, yet, for none of them is that degree of accuracy claimed which is so essential in a reliable quantitative operation. The chief objection to all of these methods is the use of an outside indicator. However, by using an inside indicator and modifying slightly the usual preliminary steps (necessary for the conversion of the ore into the sulphate) results have been obtained by the writer which are quite satisfactory.

The operation may be briefly outlined as follows: The lead is first converted into lead sulphate, then into lead acetate. Excess of standard potassium bichromate is added, which precipitates the lead as lead chromate. The unused potassium bichromate is reduced by excess of standard arsenious acid, and this latter

[1] This Journal, 17, 901; *Engineering and Mining Journal*, July 7, 1894.

titrated with iodine solution, using starch paste as an indicator.

PREPARATION AND STANDARDIZING OF SOLUTIONS.

Taking tenth normal solution of iodine as the standard, 4.995 grams of arsenious acid per liter and 4.763 grams of potassium bichromate per liter give standard solutions of equivalent value per equal volumes.

Iodine.—12.7 grams are dissolved in concentrated potassium iodide solution and made up to one liter.

Arsenious Acid.—Dissolve 4.95 grams in twenty or thirty cc. of saturated, filtered solution of sodium carbonate, gently warming. If too strong heat is applied the arsenious acid cakes and dissolves with difficulty.

By means of a burette accurately measure ten to fifteen cc. of arsenious acid solution, running it into a large porcelain dish. Acidify faintly with sulphuric acid, add fifty cc. saturated solution of pure sodium bicarbonate, add starch paste and titrate with the iodine.

Potassium Bichromate.—Weigh out approximately five grams, dissolve and make up to one liter. Remove twenty-five cc. to a porcelain dish, add fifty cc. of the standard arsenious acid and proceed with titration as already indicated.

Note.—Since all commercial sodium bicarbonate will decolorize more or less iodine, it is well in neutralizing to get the neutral point exactly. When this is attained, add fifty cc. sodium bicarbonate and deduct its iodine value from the quantity consumed.

The Operation in Detail.—Take from three to seven grams of ore, according to its richness in lead. Place this in a deep three-inch porcelain dish, thoroughly moisten it with water, cover the dish with a watch-glass and for each gram of ore used add four to five cc. of a previously prepared mixture of two parts by volume of sulphuric acid, three parts by volume of nitric acid and one part by volume of water. When the reaction, which first results, diminishes, evaporate as nearly to dryness as is possible without spurting. Cool, fill the dish with cold water, stir well and allow to settle for two or three minutes. Filter and wash with cold water until most of the acid is removed. Convey the

filter paper with the precipitate to a 300 to 400 cc. beaker or Erlenmeyer flask and neutralize any remaining acid with dilute ammonia. To the porcelain dish add ten to fifteen cc. strong ammonium acetate, made decidedly acid with acetic acid. Add an equal volume of water and boil for two or three minutes, washing the sides of dish so as to remove any remaining lead sulphate. This solution is then added to the flask containing the precipitate and the whole boiled from seven to ten minutes with frequent stirring. Cool, neutralize with ammonia, add 100 cc. of standard potassium bichromate, stirring well. Filter into a half liter measuring flask, moistening the filter paper with dilute ammonia or ammonium acetate. Wash precipitate as much as is possible in the flask, using hot water. The filtrate make up to the mark, and for titrating remove 100 cc. to a large one and one-half liter porcelain basin. Add ten to twenty cc. (or less if ore is rich in lead) of standard arsenious acid. Make decidedly acid with forty per cent. sulphuric acid and stir until the yellow color disappears or the liquid has a greenish tinge. A large excess of sulphuric acid is to be avoided. Neutralize with saturated solution of sodium bicarbonate and then add an excess of fifty cc. If the solution has a deep greenish tinge dilute it with distilled water. Finally add starch paste and titrate with standard iodine solution.

As a test of the accuracy of method, five portions of pure lead sulphate were acted upon and the following results obtained:

Grams taken.	Grams found.
1.0	1.000568
1.1	1.099375
1.2	1.200467
1.3	1.300673
1.4	1.399571

With a specimen of galena containing quartz and calcium carbonate, the writer obtained the following percentages:

Grams taken.	Per cent. lead found.
0.7	81.89
0.7	81.96
0.71	81.94
0.68	81.90

As a test of the method in the hands of inexperienced operators, it was outlined and explained to four junior students, who with the galena ore already mentioned, obtained the following results:

Grams taken.	Per cent. lead found.
R. H = 0.7	81.86
G. E. R. = 0.7	81.78
S. D. { 1 = 0.7	82.00
S. D. { 2 = 0.85	81.89
G. E. S = 0.7	81.95

With another ore containing five per cent. of copper, twenty-six per cent. of iron, quartz and gypsum, one of the students obtained the following results:

Grams taken.	Per cent. lead found.
3.0	15.89
3.5	16.01
4.0	15.97

ESTIMATION OF SULPHIDES IN CALCIUM CARBIDE.

By Fred. J. Pope.

Received May 21, 1896.

A WEIGHED quantity of calcium carbide was conveyed to a dry Erlenmeyer flask provided with a stop-cock funnel and a delivery tube, which latter led to a ten ounce wash bottle, this in turn being connected with a smaller one. The wash bottles contained 150 cc. lead acetate of known strength (about tenth normal). By means of a stop-cock water was carefully added until there was no further evolution of acetylene. On the reaction ceasing, twenty-five to forty cc. sulphuric acid (1 : 3) was run into the flask and the whole gently boiled, the liberated hydrogen sulphide passing into the wash bottles and precipitating the lead as lead sulphide. When the reaction had ceased the flask and liquid was washed free of hydrogen sulphide by a current of air and the contents of wash bottles filtered. The filtrate containing unconsumed lead acetate was made up to a half liter. To 100 cc. of this solution were added standard potassium bichromate, arsenious acid, etc., (as indicated in preceding article) and total amount of unconsumed lead acetate estimated. The difference between this

amount and the quantity of lead acetate started with gave amount precipitated by the hydrogen sulphide from which the sulphur existing as sulphide was calculated.

Grams calcium carbide taken.	Per cent. sulphur found.
2.4492	3·37
3.1234	3·57

No attempt was made to check the application of the method. It is obvious that the impure calcium carbide may have evolved other products capable of removing lead from the solution. It is the writer's intention to investigate this and other points connected with this method.

NOTE ON THE PRESENCE OF OIL IN BOILER SCALE.[1]

By Charles A. Doremus.

Received June 9, 1896.

IT is difficult to remove cylinder oils, whether pure mineral or mixtures of mineral and animal from condensed exhaust steam. The practice of recovering steam either for the preparation of distilled water or for boiler feed water is now so general that opportunities for observing the troubles attending the procedure are not wanting.

This sample of water was obtained by melting the "core" of cakes of artificial ice. The sediment is fine, flocculent and of red color. When removed from the water and dried it is pulverulent. There is very slight evidence of oil in the dry mass, the moist sediment does not appear oily. The large proportion of oil extracted by ether shows how inefficient the filters were in purifying the condensed steam. Yet very great pains were taken at the ice plant to secure pure distilled water, and there was no visible oiliness in the water as it flowed to the freezing cans. Here however the corrosive action of the distilled water on the galvanized iron produced a mass of iron and zinc hydrates which in being pushed to the centre by the gradual formation of ice gathered the oil and carried it to the core.

Another specimen is one obtained from a steamboat trafficing on the Hudson river and using salt or brackish water in the surface condensers. The boilers were said to be foul with masses

[1] Read before the New York Section, June 5th, 1886.

of oil coating the sides and tubes. Having determined the presence of the salts of sea water in the boiler, due to leaky condensers, a treatment was suggested which caused a fine precipitate. This precipitate gathered the oil in masses easily brushed from the crown sheets. When this mass is treated with ether a dry powder remains and oil dissolves.

A third specimen sent for examination from a large plant in Chicago, evaporating 2500 gallons of filtered river water and 25,000 condenser water every twenty-four hours. Lubricating oil, mineral with ten per cent. animal, is freely used, and the fine clay in the water has together with some incrusting ingredients, caused the oil to form into balls.

The next two specimens are in striking contrast to the foregoing. This is light colored, one-quarter inch thick, has a layer of dense nature near what must have been the heated surface on which the scale formed while the bulk of the incrustation is fibrous. The incrustation consists of calcium carbonate and sulphate, with which is intermingled clay and organic matter, the latter partly oil.

The general appearance of the next sample is quite different. The incrustation is in thin sheets about three-sixteenths inch thick, of light slate color, and made up of alternating layers of deposit of varying hardness. The ingredients are again calcium carbonate and sulphate and clay, while there is much organic matter. This can be separated from the mineral in great part by a little acid. The presence of oil is then noticeable. The boiler of this plant is fed with Lake Michigan water and condenser water. The latter goes directly to the hot well of twenty barrels capacity. While there are no oil filters the boiler is provided with a skimmer, which draws off floating materials from just below the water line. The lubricating oil used is mineral with fifty per cent. animal.

Notwithstanding the skimmer, the scale has formed and baked into a hard mass. It is highly non-conducting. It can be held by the fingers quite near to where a portion is heated in a Bunsen flame, the heat of which distils out and ignites the oil. A few pieces of this scale heated in an improvised retort made from a test tube yield quite a gas flame. The presence of oil

to the extent of from twenty to fifty per cent. in the deposits and scale of marine boilers filled with fresh water, any loss being made up from the exhaust or from sea water has been fully set forth by Lewes,[1] who also gives the causes thereof and remedies therefor. He also alludes to the possibilities of this type of scale forming in stationary boilers.

The specimens presented serve to illustrate the importance of critically examining the nature of the "*organic matter*" of incrustations, the statement "loss of ignition" being far too general.

[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

OCCURRENCE OF THE AMINES IN THE JUICE OF SUGAR CANE.

BY J. L. BEESON.

Received June 15, 1896.

THE presence of amines in the products of the sugar beet has long been known, but until this sugar season they have not been known to exist in the juices of sugar cane. Last December, while working with the precipitate formed by the addition of lime water to cane juice, it was noticed that the product dried at about 110° C. had a fishy odor. Upon heating some of this in a test tube over a burner, an alkaline vapor was given off which had a fishy ammoniacal odor. So about 300 grams of the dried substance was gradually heated in a hard glass retort upon a sand bath until an almost complete destructive distillation was effected. The products evolved were passed through a condenser and then through a series of U tubes, each of which was kept at a temperature a little below the boiling-points of each of the principal amines. A solid collected in the condenser tube, and an illuminating gas escaped from the last U tube, which was kept at —10° C. These products were not examined. There collected in the first receptacle about twenty cc. of an acid liquid. This was made alkaline with caustic soda and distilled. The products as before were passed through the series of tubes maintained at the different temperatures, when there

[1] *Chem. News*, 63, 181.

collected in the first, along with some water, about five cc. of clear liquid, which was strongly alkaline, had a pungent fishy odor, combined with hydrochloric acid, and otherwise manifested the general properties of the amines. An attempt was made to further purify it by freeing it from the water, but the amount was too small to bring to a definite boiling-point. The remaining liquid was neutralized with hydrochloric acid, and slowly evaporated down, whereupon a few crystals, slightly colored and deliquescent, were obtained. The quantity was too small to admit of an elementary analysis, so it was not possible to say whether the product was a single amine or a mixture of amines. The filter cake, the refuse from the clarification of cane juice, gave the same odor and alkaline vapor upon heating. It was my aim to subject several pounds of the filter cake to the same treatment in order to fully clear up the question, if possible, but the amount of other work required of me prevented. The clearing up of the matter is of the greatest scientific and practical interest to the sugar industry, as it will doubtless throw light upon the nature both of the amido and albuminous bodies of the cane juice. I write the account of the work with the hope that some chemist may be induced to continue the work, as the writer will discontinue sugar work.

[CONTRIBUTED FROM THE LABORATORY OF THE LOUISIANA EXPERIMENT STATION AND SUGAR SCHOOL.]

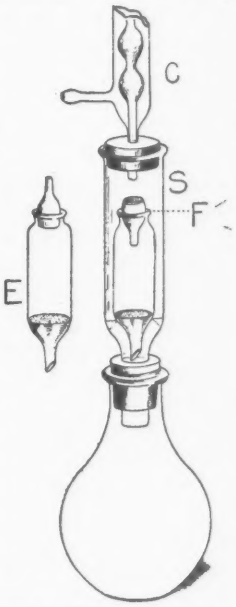
A SIMPLE AND CONVENIENT EXTRACTION APPARATUS FOR FOOD-STUFF ANALYSIS.

BY J. L. BEESON.

Received June 15, 1896.

THE apparatus shown in the accompanying illustration I have adapted from the Johnston extractor, for the general use of the average student in the laboratory aiming at simplicity, greater compactness, convenience, rapidity of operation, and accuracy. The extraction tube *E*, which is rather short, is provided as usual with a perforated platinum disk fused into the bottom, and in addition with a specially devised funnel stopper of ground glass, by means of which the weighed sample can be rapidly

and effectively dried to constant weight in a current of dry hydrogen or other inactive gas for the estimation of the moisture, and at the same time preparing the sample for extraction. Rubber caps are placed over the two ends of the tube during the cooling and weighing. For the extraction of the sample, the tube *E* is placed in a Stutzer tube *S* as shown in the figure, which is connected as usual with an ether flask below, and by means of either a cork or mercury joint with a short bulb condenser above. The funnel stopper, placed as shown, directs the returning drops of the liquid upon the center of the sample, and especially it prevents the loss of the sample by spattering. This is a source of objection to all forms of open extractors. Owing to the very small percentage of fats or ether extracts in most food stuffs a small loss of the sample from this cause makes a very large analytical error in the work, whether estimated from loss of the sample or gain in weight of the ether flask. During two years use in this laboratory we have obtained with the apparatus very concordant results between duplicate analyses, and would commend it for the use of students especially. By means of a seven mm. glass tube, six tubes and samples are dried in a current of hydrogen at a time in a water-oven. The whole apparatus may be had of Max Kaehler and Martini, Berlin.



NEW BOOKS.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS. By BERTRAM BLOUNT AND A. G. BLOXAM. In two volumes. VOLUME I, CHEMISTRY OF ENGINEERING, BUILDING AND METALLURGY. 8vo. 244 pp. London: Charles Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co.

This work is a compilation of material intended to cover the chief branches of chemical industry. The first volume deals in

the first part with the chemistry of building materials, fuel, steam making and lubrication. The second part is entirely devoted to metallurgy.

The scope of the work necessitates condensation, yet the reader will be impressed at times with the meagerness of description, especially as the treatment of other subjects seems disproportionately extended. An appearance of unevenness in treatment is thus given, which might have been avoided.

Books of this class are more difficult to write as the limits of technical science are widened and there is room for much judgment in holding a proper balance between the necessities of the reader and the restricted space of a hand book or text book. While this book will be very serviceable to the large class of engineers and manufacturers for whom it is especially written, and even to the student of industrial chemistry, it can hardly be of much interest to " the expert in any one of the branches touched upon" (*vide* preface). The touch is entirely too light as a rule for those who seek extended information. The entire absence of references, also, deprives the work of much of the usefulness it might have had for professional readers in subjects not strictly their own.

The illustrations are good as far as they go, but are much less freely supplied than the nature of the book requires.

The subjects of gaseous fuel and water for steam making are well and clearly treated. Of boiler compositions the authors justly say that " none should be used without a knowledge both of its composition and of that of the water to be treated," and that, " all are sold at prices bearing but a remote relation to their intrinsic values." As to the preservation of iron by paint, the statement that red lead paint is the best will hardly meet unqualified assent.

The treatment of the metallurgy of iron is very full, and contains a good though brief discussion of the influence of foreign elements on the quality of iron. The statement that "the chief gold-producing countries are Australia, America (California), and Russia" is more compact than edifying. Electrometallurgical processes are given in treating of many of the metals. The commercial production of aluminum is described

briefly but no allusion is made to the part which the United States have played in the development of this industry, nor do the names of Cowles or Hall appear in the text.

The second volume will treat of the chief chemical industries other than those referred to.

A. A. BRENEMAN.

LABORATORY EXPERIMENTS IN GENERAL CHEMISTRY. By CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

EXPERIMENTS IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS. By CHARLES R. SANGER, A.M., PH.D. Paper. St. Louis. Published by the Author. 1896.

These two little books by Professor Sanger contain well selected collections of experiments for beginners in chemistry. The first collection was prepared for students in a general college course, while the second collection appears to have been arranged for students beginning a medical course. In the first collection for college students there is evidence that the author had in mind the needs of those who spend but part of a year in the laboratory. What the student is told to do is clearly indicated and his attention is directed at every step to the important points in the reactions considered. The experimental course offered to medical students is not as extended as the present writer would like to see, but is as full as this class of students is supposed to need, and has, besides, the advantage of systematic arrangement.

J. H. LONG.

BOOKS RECEIVED.

Eighth Annual Report of the Kentucky Agricultural Experiment Station of the State College of Kentucky, for the year 1895. Lexington, Ky. lxvi, 150 pp.

North Carolina Weather during the Year 1895. North Carolina Agricultural Experiment Station, Raleigh, N. C. lii, 264 pp.

Bulletin No. 122. Cost of Nitrogen, Phosphoric Acid and Potash. Proper Use of Tables of Analysis of Fertilizers. Connecticut Agricultural Experiment Station, New Haven, Conn. 16 pp.

Reduction of Nitrates by Bacteria and Consequent Loss of Nitrogen. By Ellen H. Richards and George William Rolfe. 20 pp. Reprinted from the *Technology Quarterly*, Vol. IX, No. 1, March, 1896.

Nitro-Explosives. A Practical Treatise. By P. Gerald Sanford, F. I. C.,

F. C. S. London: Crosby, Lockwood & Son. 1896. xii, 270 pp. Price, 9s.

Embalming and Embalming Fluids, with the Bibliography of Embalming. Thesis by Charles W. McCurdy, Sc.D., Ph.D. Wooster, Ohio: The Herald Publishing Co. April, 1896. 84 pp.

Bulletin No. 64. Analysis of Commercial Fertilizers. Kentucky Agricultural Experiment Station of the State of Kentucky, Lexington, Ky. July, 1896. 16 pp.

OBITUARY NOTE.

PETER COLLIER, Ph.D., was born in Chittenango, New York, August 17, 1835. He graduated A.B. at Yale College in 1861 and later Ph.D. He also graduated at the Sheffield Scientific School, and was for some time an assistant and instructor in that School. From 1867 to 1877, he was Professor of Physics and Chemistry in the University of Vermont, and also Professor of Chemistry in the Medical Department of that University, and for some time Dean of the Medical Faculty. In 1873 he was appointed one of seven scientific commissioners to the Vienna Exposition, by President Grant. From 1877 to 1882 he was Chief Chemist to the Department of Agriculture of the United States, at Washington. During his official term, he gave very great attention to the problems of cultivating sorghum and manufacturing sugar from it. From 1882 to 1885 he still remained in Washington, engaged in chemical pursuits and writing for scientific and agricultural publications. From 1887 to 1895 he was Director of the New York State Experiment Station at Geneva, New York, where he instituted much experimental work especially upon fertilizers and dairy problems. He had a wide acquaintance with scientific men, and himself possessed great energy and force. Illness obliged him to resign his position last year and he came to Ann Arbor last December. He died on June 29.

A. B. PRESCOTT.

ERRATA.

On page 651, July number, 15th line from top, for 159,000 *read* 166,000.
On page 653, 7th line from bottom, for 159,000 *read* 166,000.
On page 654, 4th line from top, for 136,519.5 *read* 116,519.5.